ATTACHMENT E.3

FEMP HISTORICAL ENVIRONMENTAL RELEASES

FEMP RECYCLED URANIUM RELEASES TO THE ENVIRONMENT

Attachment 3 to Appendix E for the DOE Ohio Sites Recycled Uranium Report presents published work by others that document and discuss the potential releases of recycled uranium to the environment. Appendix E, Attachment 3.1 was originally compiled as Appendix F.3, Attachment I in the FEMP Operable Unit 5 Remedial Investigation Report issued in February 1995. This appendix methodically compiles and analyzes airborne releases during the entire 35+ years of operation of the FEMP. This data and text was carefully edited to remove, to the extent practical, the discussion and inclusion of airborne release data prior to 1961 and the resulting edits form the basis for the text presented in Section 2.5.

Appendix E, Attachment 3.2 was originally compiled and published by *Radiological Assessments Corporation* under its Tasks 2 and 3 work on "The Fernald Dosimetry Reconstruction Project". This text and data provided the best available information and was, therefore, used to develop a brief discussion of liquid releases to the environment from FEMP operations.

ATTACHMENT E.3.1

FEMP ENVIRONMENTAL RELEASES VIA AIRBORNE PATHWAY

(OPERABLE UNIT 5 RI REPORT

APPENDIX F.3, ATTACHMENT 1)

APPENDIX F.3

ATTACHMENT I

HISTORICAL AIRBORNE RELEASE OF URANIUM

AND

GEOCHEMICAL CONCEPTS OF THE SUBSURFACE URANIUM DISTRIBUTION

AT THE FERNALD SITE

F.3.I.1.0 INTRODUCTION

Remediation of uranium-contaminated soil is considered a high priority at the Fernald Environmental Management Project (FEMP). The concepts of leaching and subsequent transport of uranium must be understood for predicting the environmental impact this soil could potentially have on the underlying groundwater quality in the Great Miami Aquifer. This report was prepared to summarize historical airborne uranium releases, type of deposition, form of uranium, and the geochemical conditions which have and will affect uranium migration through the soil column. Finally, this report relates these concepts to the leaching and distribution coefficients (K_l and K_d) used in the uranium fate and transport model for the Operable Unit 5 Remedial Investigation (RI) Report.

Historical releases of uranium are covered in Section F.3.I.2.0 to introduce the forms of uranium present in the existing source areas. In general, uranium releases from the process plants at the site have occurred in the past either as repetitive emissions or as singular, and in some instances, episodic, well-documented events. An example of a singular airborne release is the 1966 UF_6 tank leak at the pilot plant. Episodic UF_6 releases occurred at Plant 7 in the mid-1950s and repetitive airborne releases of various forms of uranium oxide have been emitted from Plants 2/3, 4, and 5. Examples of former repetitive point source releases to the soil are acid bath spills at Plants 2/3, 6, and 8.

In Section F.3.I.3.0, the mobilization of the various uranium forms in the source will be examined from a geochemical perspective. Rainwater will leach the various uranium forms and both dissolved and particulate forms will migrate downward through the soil column with infiltrating rainwater. In general, the soil column is dominated by carbonate minerals in the glacial overburden which is predominently highly fractured and weathered (brown) glacial overburden in the upper 8 to 15 feet of the column underlain by dense gray glacial overburden to a depth of 20 to 50 feet across most of the site. Fractured glacial overburden has a brown appearance due to the oxidation of iron, as this sediment and groundwater are in contact with oxygen in the atmosphere. The gray glacial overburden has not been oxidized because the absence of fractures eliminates the principal atmospheric pathway for oxygen exchange. Dissolution reactions between rainwater and carbonate minerals are the primary control on the porewater and groundwater compositions, resulting in carbonate-rich waters that is effective at complexing and transporting uranium. Adsorption of uranium by the weathered

and unweathered glacial overburden is not significantly different, as the aqueous form of uranium is homogenous throughout the glacial overburden. The surface of the water table in the glacial overburden is about 3 to 5 feet below land surface.

Below the glacial overburden is the highly permeable sand and gravel that contain the Great Miami Aquifer. Due to the high hydraulic conductivity contrast between the glacial overburden and the upper portion of the sand and gravel is unsaturated and the Great Miami Aquifer exists as a second unconfined water table as much as 45 feet below the bottom of the glacial overburden. The composition of groundwater in the Great Miami Aquifer is very similar to groundwater in the glacial overburden. Therefore, the nature and mobility of uranium species in these groundwaters is similar.

Airborne releases of uranium particles have been deposited site wide on the surface of the soil as both highly soluble uranium fluorides and less soluble uranium oxides. Over the 1951 to 1989 period of operation, the uranium fluoride forms in this air-deposited source have been leached and transported into the soil column by infiltrating rainfall. Additionally, uranium oxide particles may have been suspended and carried into the subsurface by infiltrating rainwater. The aqueous uranium derived primarily from dissolution of the uranum fluoride forms migrated into the soil first and the less soluble uranium oxide particles remained at or near the surface. As time progresses, the uranium fluoride forms are depleted from the source and uranium concentrations in the infiltrating rainfall begin to decrease, as the less soluble uranium oxide particles become the primary source for leaching. The nature and extent of these migrating fronts with respect to past, present, and future distribution of uranium is evaluated in Section F.3.I.4.0.

Section F.3.I.5.0 of this report will relate the historical releases and geochemical concepts to the leaching and distribution coefficients (K_l and K_d) used in the uranium fate and transport model for the Operable Unit 5 RI Report. Leaching coefficients are used to determine the input uranium loading as a function of time, and the large range in observed and calculated values (about 1 to 3500 L/kg) reflects the heterogeneity of uranium forms in the source. In contrast, the large range in distribution coefficients (about 1 to 2400 L/kg) reflects the kinetics of adsorption versus desorption, rather than a variety of uranium forms. Adsorption distribution coefficients are well constrained to the range of 11 to 40 L/kg, while desorption coefficients vary from 75 to 2433 L/kg. The lower adsorption values are used to model uranium migration when the source is present, and desorption coefficients are applicable once the source has been removed.

F.3.I.2.0 AIRBORNE RELEASE HISTORY

Uranium releases at the FEMP (known until 1991 as the Feed Materials Production Center) are addressed in this section through discussions of the release mechanisms, routine discharges from production operations, significant episodic releases from plant operations, and nonproduction source releases of primary contamination.

F.3.I.2.1 AIRBORNE RELEASE MECHANISMS

The major features of the FEMP are illustrated in Figure F.3.I.2-1. Plant process operations were limited to a fenced, 136-acre tract known as the production area. Liquid and solid wastes that were generated by the various chemical and metallurgical processes were stored or disposed of in the waste storage area located west of the production area. The cessation of production operations in 1989 essentially eliminated further primary releases to environmental media; secondary release mechanisms and resultant contaminant migration are continuing.

Several mechanisms of airborne release exist for the transport of radiological contaminants to environmental media primarily from process operations and waste management practices. Secondary releases, such as air resuspension of contaminated soil, contributed to further migration and likely transport to other media as outlined in Table F.3.I.2-1.

F.3.I.2.1.1 Primary Discharges From Production Operations

Uranium processing operations within the FEMP production cycle resulted in both routine and episodic primary releases of airborne radiological contaminants to environmental media. Airborne particles and gases were generated during most production, storage and handling operations over some 38 years of processing uranium materials. The principal sources of routine airborne emissions from process operations were dust collector discharges, wet scrubber discharges, and acid-pickling fume stacks. Episodic releases resulted from unplanned incidents arising from either human error, equipment malfunctions, procedures, or situational conditions.

F.3.I.2.1.2 Secondary Releases From Nonproduction Sources

Emissions of uranium from nonproduction sources included those from waste management storage practices, incinerator operations and building exhausts. Fugitive dust generated from the waste

storage pits can be attributed to load-in/load-out operations, wind erosion of stored materials, and

vehicle movement in the storage area. Five nonproduction solid/liquid waste incinerators supported

the general site operations. Exhausts from buildings located within the production area and the

laboratory contributed uranium releases.

F.3.I.2.2 ROUTINE DISCHARGES FROM PRODUCTION OPERATIONS

Routine operations at the FEMP resulted in occasional discharges from the process stacks and

by-products, which were handled in a variety of ways. Figure F.3.I.2-2 is a schematic flow diagram

of the FEMP process and identifies the major products by each plant. Contamination of

environmental media resulted from releases during process operations and from handling and

disposition of the by-products that were treated as waste streams. Descriptions of process operations

and waste management practices are presented from a broad perspective of how these activities

contaminated the environmental media.

The total airborne emissions since operations began in 1951 amount to 179,318 kilograms of uranium

(kg U), and are compiled in Table F.3.I.2-2. The total releases are determined by summing the

estimated and measured uranium emissions from a number of process stacks and vents. For the

purpose of analysis, releases through 1984 were considered inasmuch as airborne emissions beyond

that time were relatively insignificant. Uranium discharges from monitored stacks were the only

measured emissions. Table F.3.I.2-2 summarizes the annual airborne emissions from all sources at

the FEMP since operations were started in the 1950s.

F.3.I.2.2.1 Description of Plant-by-Plant Operations and History

The FEMP began operations in 1951 upon completion of the pilot plant, the site's first operational

facility. This plant served as the prototype for the entire FEMP process during the design and

construction of the other plants. Plant 6 began operations in 1952, followed by Plants 1, 2/3, 4, 5

and 8 in 1953. Plants 7 and 9 became operational in 1954. Production peaked in 1960 at

approximately 12,000,000 kg U. A product decline began in 1964 and reached a low of 1,230,000

kg U in 1975.

The following paragraphs provide an overview of the chemical and metallurgical processes used at the

FEMP for the manufacture of uranium metal products (Figure F.3.I.2-3). In general, these processes

occurred in seven of the FEMP's more than 50 production, storage and support buildings. Emphasis

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is placed on the process chemistry, equipment and uranium species discharged as primary airborne releases during different periods of operation.

F.3.I.2.2.1.1 Plant 1 (Sampling Plant)

Operations began in 1951 for the sampling of impure uranium feed materials. The plant received large quantities of natural, enriched and depleted uranium materials which were sampled and analyzed for uranium assay and isotopic enrichment. Drummed K-65 materials were temporarily stored on the Plant 1 pad in the early 1950s. The plant had 15 dust collectors; dust particles were generally 8 to 24 microns in size and in the form of uranium ores concentrates, and oxides.

F.3.I.2.2.1.2 Plant 2/3 (Refinery)

Operations began in 1953 for the conversion of impure feed materials (received from Plant 1) to pure uranium trioxide (UO_3). This was accomplished by dissolving the feeds in nitric acid; purification by solvent extraction; and thermal decomposition of the purified uranyl nitrate hexahydrate (UNH) solution to produce UO_3, commonly called orange oxide.

Plant 2/3 processed three classes of materials: pitchblende ores as they were mined and shipped to the FEMP; domestic uranium concentrates that had undergone a preliminary refining process at the mill sites; and residues recovered at various stages of FEMP operations. Pitchblende ores contained elevated levels of radium and were processed from 1953 to 1955.

Beginning in 1962, Plant 2/3 was used for processing quantities of residues that were generated by the FEMP processing plants along with those received from several U.S. Department of Energy (DOE) facilities. Residing within the residues received from off site were trace quantities of fission products and transuranics. These feed streams generally contained less than 3 parts per billion (ppb) of transuranics such as plutonium (Pu)-239 and less than 10 parts per million (ppm) of fission products such as technetium (Tc)-99. Plant 2/3 contained four dust collectors and two scrubbers. Releases included small UO_3 particles which penetrated the scrubbers, UNH, and radium (Ra)-226.

F.3.I.2.2.1.3 Plant 4 (Green Salt Plant)

Operations began in 1953 for the conversion of pure UO_3 (received from Plant 2/3) to pure uranium tetrafluoride (UF_4), commonly called green salt. This was accomplished by a two-step process that reduced UO_3 with hydrogen to form uranium dioxide (UO_2), which was then converted to UF_4 by

reaction with anhydrous hydrogen fluoride. Plant 4 contained 12 dust collectors. Dust particles were 2 to 22 microns in size and ranged from 50 to 81 percent uranium (UO_2, UO_3, U_3O_8, and UF_4). Discharges of UF_4 are estimated to contain 2 percent UO_2F_2, a uranium species side product from the Plant 4 process.

F.3.I.2.2.1.4 Plant 5 (Metals Production Plant)

Operations began in 1953 for the conversion of pure UF_4 (received from Plant 4) to uranium metal derbies by high-temperature reduction using magnesium metals granules. After heating for 3 to 4 hours at approximately 1200°F, the UF_4 and the magnesium would initiate an exothermic reaction. The resulting product was a 300- to 375-pound piece of pure uranium metal and a by-product, magnesium fluoride slag. The resultant piece of uranium metal had the shape of a gentleman's hat, or derby; therefore, these pieces were called derbies. Most of the derbies were recast to form ingots for further processing at the FEMP, but some were shipped directly or cast into flat billets. Graphite crucibles were machined and the magnesium fluoride slag milled for reuse in reduction pots. Plant 5 contained 17 dust collectors. Dusts in the reduction area were mostly UF_4 and U_3O_8 in magnesium fluoride slag. Remelt area dusts were mostly U_3O_8. Dust particles were 0.5 to >44 microns in size.

F.3.I.2.2.1.5 Plant 6 (Metals Fabrication Plant)

Operations began in 1952 for the fabrication of finished cores from normal uranium cylindrical ingots received from Plant 5 via rolling mill, heat treat and machining operations. Later, enriched and depleted uranium ingots were machined in Plant 9 and heat treated in Plant 6 for shipment to Reactive Metals, Inc. (RMI) Company located in Ashtabula, Ohio. At RMI, uranium ingots were extruded into tubes for return to Plant 6 at the FEMP where they were cut into sections, heat treated, machined to final dimensions, and inspected for final product quality. The completed target element cores were shipped to the Savannah River Plant. Ingots consisting of slightly enriched uranium were upset forged, machined, and shipped from RMI to the Hanford site. Scrap metal that was generated during the various metal production and fabrication steps was pickled in nitric acid to remove oxide contamination and progeny products before recycling via remelt casting operations. Chips and lathe turnings were crushed, pickled, rinsed, dried, briquetted, and recycled to remelt casting operations. Plant 6 contained three dust collectors and three electrostatic precipitators. The principal airborne emission path from Plant 6 was the acid-vapor exhaust from the stack that ventilated the pickling tank, two wash tanks, and the exhaust from the briquetting operations.

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F.3.I.2.2.1.6 Plant 7 (Hex Reduction Plant)

Operations began in 1954 for the conversion of UF_6 received from the gaseous diffusion plants to produce high purity UF_4 as a supplement to the Plant 4 production. Actual production ran from 1954 to 1956; the plant contained four dust collectors.

F.3.I.2.2.1.7 Plant 8 (Scrap Recovery Plant)

Operations began in 1953. Plant 8 processed impure metals and residues including off-specification UO_3 and UF_4, magnesium fluoride slag, crucible burnout, ingot top crops, sump cakes, chips, and sawdust received from nearly all the production plants. High-grade scrap, such as machining chips and turnings, were oxidized to U_3O_8 in an oxidation furnace or burned in a box furnace. Fine material (<8 mesh) was sent to Plant 2/3; coarse material (>8 mesh) was further oxidized in a muffle furnace. The furnaces were vented to wet scrubbers before gases were discharged to the atmosphere.

F.3.I.2.2.1.8 Plant 9 (Special Products Plant)

Uranium operations began in 1957. Plant 9 originally conducted casting and cropping of ingots from Plant 5. Cropped billets from Plant 5 were drilled and machined for further processing in Plant 6. Beginning in 1961, the Zirnlo process was used to recover rejected coextrusion sections from the fuel fabrication operation at Hanford. The process used dilute hydrofluoric acid to remove zirconium followed by nitric acid for copper removal from uranium cores. The decladded cores were then recycled through Plant 5 remelt casting operations. The acid tanks had an exhaust stack with a blower. Core pickling was used from 1961 to 1963; briquetting of uranium and thorium was performed from 1953 to 1963.

F.3.I.2.2.1.9 Pilot Plant

Operations began in 1951. During the early years, the pilot plant produced limited quantities of enriched uranium metal. Box furnaces were used to process U_3O_8, enriched uranium turnings and "sawdust" generated in the production of enriched uranium cores. Crucibles were plasma coated in the pilot plant. Material up to 3.85 percent enrichment was processed to metal via the UF_6 reduction process. Most uranium operations were suspended during the thorium production that occurred between 1967 and 1975.

Conversion of UF_6 to uranium tetrafluoride (UF_4) began by heating the UF_6 in an autoclave to transform the solid into a gas. The gaseous UF_6 was then reduced with hydrogen to form UF_4. The UF_4 was feed material for Plants 5 and 9. The c····s from the production of UF_4 consisted of hydrogen, nitrogen, hydrogen fluoride, uranium fluoride, a carbon trap to remove unreacted uranium hexafluoride, a two-stage refrigerated condenser system to remove anhydrous hydrogen fluoride, and a water scrubber to remove trace aqueous hydrofluoric acid before being vented to the atmosphere. Equipment in the pilot plant was used for a variety of special production operations. The dust from the collectors in the pilot plant was 9 to 44 microns in size and assayed approximately 80 percent uranium in the form of UO_3, U_3O_8, and UF_4.

F.3.I.2.2.2 Time/Form Characterization of Plant Discharges

The principal sources of airborne emissions from FEMP processing operations were:

- Dust collector stack discharges
- Wet scrubber disch····es
- Acid-pickling fume stacks.

Airborne releases from these sou··es totaled 169,147 kg U through 1984, and are characterized in the following subsections.

When combined with the release of 8891 kg U from nonproduction sources (Sections F.3.I.2.3 and F.3.I.2.4), the FEMP total comes to 178,038 kg U through 1984 (see Table F.3.I.2-2).

F.3.I.2.2.2.1 Dust Collector Stack Discharges

Dust collector stack discharges were the principal sources of airborne emissions during the span of FEMP operations from 1951 to 1984. Airborne releases of uranium from plant stacks totaled 94,590 kg U and are characterized as follows:

Plant	Stacks (kg U)	Percent	Principal U Species
1	985	1	U Ores, U_3O_8
2/3	3219*	3	U Ores, U_3O_8, UO_3
4	33,217	35	UO_3, U_3O_8, UF_4/UO_2F_2
5	26,189	28	U_3O_8, UF_4/UO_2F_2
6	1204	1	U_3O_8

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Plant	Stacks (kg U)	Percent	Principal U Species
7	13,272	14	UF_4
8	10,773	12	U_3O_8, UAP, UCl_4
9	2599	3	U_3O_8, UF_4/UO_2F_2
Pilot**	3132	3	U_3O_8, UF_4
Total	94,590	100	

*Estimated releases due to gulping operations (38179.3 kg U) have been subtracted from the Table F.3.I.2-2 total for Plant 2/3 and will be covered in Section F.3.I.2.2.2.2.

**Estimated episodic release in 1966 (1195 kg) was subtracted from Table F.3.I.2-2 total for the pilot plant because it was not released through the dust collector stacks.

The Plant 8 scrubbers discharged another 36,378 kg U, primarily in the form of uranyl ammonium phosphate (UAP) and uranous tetrachloride from the dissolution of U-metal in hydrochloric acid. Each plant discharged dust as uranium residues from processing operations. Plants 4, 5, and 9 discharged UO_2F_2 as a companion side-product contained in UF_4. Estimates of dust collector discharges from all FEMP processing plants categorized by U species follow:

Uranium Species	kg U	Percent of Total
Ores	3590	4
U_3O_8, UO_2	66,649	70
UO_3	149	<1
UF_4	23,387	25
UO_2F_2	194	<1
UCl_4	28	<1
UAP*, ADU**	593	<1
Total	94,590	

*Uranyl ammonium phosphate
**Diammonium diuranate

Ninety-five percent of the discharges were oxides and green salt. Stack discharges from Plants 4 and 5 comprised 63 percent of the total discharged from the FEMP processing plants. It should be noted that dust collector discharges from Plants 2/3 and 8, when combined with emissions from gulping operations and the wet scrubber discharges, together accounted for 52 percent (88,549 kg U),

as discussed in Section F.3.I.2.2.2.2. Also, Plant 7 discharged 14 percent of the FEMP total in just three years of its operation between 1954-56. Most of the FEMP releases occurred during the first 20 years of plant operations (Section F.3.I.2.2.2.3). A breakdown of uranium stack discharges by plant, species and time is summarized in Table F.3.I.2-3.

F.3.I.2.2.2.2 Wet Scrubber and Acid-Pickling Discharges

Wet scrubber discharges over the four decades of FEMP operations resulted from Plant 2/3 gulping operations and wet scrubbers in Plant 8. Acid-pickling operations in Plants 6 and 9 further contributed to these uranium emissions. Releases of 38,179 kg U as uranyl nitrate are estimated from the Plant 2/3 gulping operations (Table F.3.I.2-4) and 36,378 kg U from the Plant 8 wet scrubbers (Table F.3.I.2-2). Emissions from the Plant 6 and 9 acid-pickling sources are judged to be relatively insignificant. The impact of these emissions to the environmental media is in the discharge of acidic vapors that are conducive to promoting solub... ...tion of particulate uranium species released from other sources.

F.3.I.2.2.2.3 Historical Discharges of FEMP Dust Collector and Wet Scrubbers

Historical discharges of FEMP dust collector and wet scrubbers are listed below:

Plant	Discharges (kg U)				
	1950s	1960s	1970s	1980s	Total
1	642	252	57	34	985
2/3	14,556	13,249	12,804	789	41,398
4	27,861	4350	336	670	33,217
5	22,978	2407	332	472	26,189
6	449	751	2	2	1204
7	13,272	0	0	0	13,272
8	12,251	21,675	1952	273	47,151
9	1096	1159	168	176	2599
Pilot	1934	1179	13	6	3132
Total	95,039	56,022	15,664	2422	169,147
Percent	37	33	9	1	100

The significance of the time characterization is that the substantial quantities of uranium discharged during the initial years of operation have had ample opportunity to come into solubility equilibrium

with environmental media, undergo slow hydrolysis to other uranium species, or have migrated by transport to other media.

F.3.1.2.2.3   Dose Reconstruction Project Release Estimates

In November 1993 a draft report entitled "The Fernald Dosimetry Reconstruction Project — Radionuclide Source Terms and Uncertainties" was issued for review by the Radiological Assessments Corporation (RAC) under contract to the Centers for Disease Control (CDC). The report was prepared to support an initiative being undertaken by the CDC to reconstruct the potential radiological doses received by members of the public residing around the FEMP as a result of environmental discharges during the facility's 38-year operational history.

Within the draft CDC report, RAC evaluated the projected quantities and characteristics of radiological contaminants released to the environment from facility operations. Existing FEMP historical release estimates, as presented in the DOE's remedial investigation/feasibility study (RI/FS) documents, were based upon an evaluation of historical stack monitoring data and production records by FEMP scientific staff members. The RAC estimates employed a probabilistic approach to projecting these same historical release levels.

The probabilistic-based estimates completed by RAC included use of Monte Carlo methods to evaluate the propagation of uncertainty in the estimating process. These Monte Carlo simulations were completed for total site dust collector emissions, Plant 8 scrubber emissions, Plant 2/3 scrubber discharges, and radon released from the site. In general, the best estimate of the mass of releases from these sources, as projected by RAC, were, on average, approximately 250 percent higher than similar estimates completed by the FEMP. The primary differences reside in the estimation of releases from the Plant 8 scrubbers (385 percent higher release estimates) and the site-wide dust collection systems (265 percent higher emission estimates).

No attempt has been made to reconcile the differences between the two estimates of total mass of historical site emissions. For the purposes of this report, it is the types of uranium chemical forms (species) that are of significance to the report's findings, not the total mass of contaminants released. The differences in projected total quantities of emissions is not considered significant to the identification of geochemical parameters for fate and transport modeling, which is dependent on the species of uranium forms historically released.

F.3.I.2.3 SIGNIFICANT EPISODIC RELEASES FROM PLANT OPERATIONS

F.3.I.2.3.1 Plant 7 Releases of UF_6 in 1954-55

Eyewitness accounts have stated frequent releases of UF_6 during the start-up and early operation of Plant 7 in the 1954 period. During these incidents, building windows were closed and laboratory ventilation hoods were shutdown until the visible white plume of UF_6 dissipated from cylinders placed on-line for operations. Quantities released as UF_6 have been estimated to be 252 kg U during the operation of Plant 7.

F.3.I.2.3.2 Pilot Plant Releases of UF_6 in 1966

On February 14, 1966, an unmonitored release of 1195 kg U as UF_6 occurred during a one-hour period, beginning at 8:40 a.m. At that time winds were from the north/northwest at 5 mph. The release point was about 6 feet above the ground and resulted from a valve being inadvertently removed. Releases of another 264 kg U have been estimated for other intermittent periods of operation.

F.3.I.2.3.3 Plant 2/3 Releases of UNH/Nitric Acid Vapor

Quantities of uranium were emitted from the Plant 2/3 gulping system as a vapor mist of UNH solution in nitric acid. These emissions occurred when UO_3 was removed by vacuum gulping from denitration pots. Estimates of 38,179 kg U discharged were based on uranium production records, measurements of U content in acid mists, and collection efficiency expected from the entire particulate control system. Releases totaling 272 kg U have been estimated based on two specifically documented incidents.

F.3.I.2.3.4 Other Nonroutine Production Discharges

Emissions of uranium from metal fires and solid spills occurring outdoors have been estimated to be 907 kg U and 1059 kg U, respectively, over the period of FEMP operations through 1984. Uranium metal fires generally occurred on the east storage pads of Plants 6 and 8, where drums of machining chips and turnings were stored for the pickling and briquetting operations. Outdoor spills amounting to 37 kg U occurred during the interplant shipment of uranium compounds, usually from a drum falling from a transport trailer.

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F.3.1.2.4 <u>NONPRODUCTION SOURCE RELEASES OF PRIMARY CONTAMINATION</u>

F.3.1.2.4.1 <u>Incineration</u>

Five nonproduction incinerators supported the general site operations. Discharges from these incinerators were as follows;

- Old solid waste incinerator at the sewage treatment plant (2480 kg U)
- Oil burner (463 kg U)
- Graphite burner (125 kg U)
- New solid waste incinerator (12 kg U)
- Liquid organic waste incinerator (17 kg U)

555 Uranium releases from these sources are estimated to be 3087 kg U (Table F.3.1.2-2) for the FEMP's operational period. The likely form of airborne discharges from the five nonproduction burners and incinerators is U_3O_8 because these units functioned to oxidize the lower oxidation state uranium compounds. The oil burner and liquid waste incinerator processed hydrocarbons whose residue could have contained phosphorus in a uranium oxide matrix. Likewise, the old solid waste incinerator could have contained phosphorus plus metal oxides in a uranium oxide matrix. The graphite burner operated only on contaminated graphite and only yielded U_3O_8 as the carbon burned off. The new solid waste incinerator operated mostly on miscellaneous contaminated trash (paper, cardboard, wood, etc.) that yielded only U_3O_8. Any lower oxidation state uranium compound would not remain after processing under incineration conditions of heat and air. It is possible that quantities of phosphorus or fluoride compounds would exist to some extent given that a wide variety of chemical processing took place, but the likely form of release is U_3O_8.

F.3.1.2.4.2 <u>Storage</u>

Up to 1984, on-property disposal of solid and slurried wastes at the FEMP occurred in pits and silos. Transport of solid wastes to the pits was dependent on the type of wastes generated and the type of storage containers. In general, drummed wastes were transported on flat-bed trailers; metal dumpsters were carried by dumpster vehicles; bulk wastes were transported by dump trucks and trailers; and drummed pyrophoric metal was conveyed on four-wheeled flat-bed trailers pulled by two tractors. At the waste storage area, dump trucks, dump trailers, dumpster units, and drummed wastes were emptied directly onto the pits' edges. The material was then pushed into the pits by either a bulldozer or a dragline scraper. Loose contamination was washed from bulldozers, the dragline scraper, vehicles, dumpsters, and fork trucks with water at the pits. Fugitive airborne uranium

emissions at the waste pits have been estimated to be 1371 kg U for the FEMP operational period through 1984 (Table F.3.I.2-4).

F.3.I.2.4.3 Other Emissions

Estimates of uranium releases from building exhausts and laboratory emissions have been estimated to be 379 kg U and 68 kg U, respectively, for the FEMP operational period through 1984 (columns numbered 4 and 5, Table F.3.I.2-4). The likely form of release is U_3O_8 or intermediate uranium compounds specific to each processing plant.

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TABLE F.3.1.2-1

SUMMARY OF SITE CONTAMINATION

Potential Source	Release Mechanisms	Affected Media/Pathways

Process Operations (OU3)
    Dust collectors
    Scrubbers
    Fugitive emissions
    Wastewater discharges
    Storm water discharges
    Process material handling
    Underground storage tanks
    Process piping
    Sewage treatment plant
	Air emissions
	    Process emissions
	    Building exhausts
	    Fugitive emissions
	
	Wastewater/storm water discharges
	
	Land disposal/storage practices
		Air
		    Suspended particulates
		    Radon gas
		
		        | → Direct radiation
		        | → Air resuspension
		Soil |
		        | → Groundwater via leaching
		        | → Storm water runoff
		                  ↓
		            Surface water/sediment
		                  ↓
		            Groundwater recharge

Waste Management
    OU1
    OU2
    OU4
    Regulated units
    Soil/debris piles
    Scrap metal piles
	Spills/Leaks
	    Process materials
	    Wastewater
		Surface water/sediment
		                  ↓
		            Groundwater recharge
		
		Direct radiation

TABLE F.3.1.2-2

URANIUM EMISSIONS FROM FEMP AIRBORNE RELEASES

| | Uranium Emissions (kg) by Source | | | | | | | | | | | | | | |
| | Dust Collectors | | | | | | | | | | Plant 8 Wet Scrubbers[b] | Non-production Sources[c] | Other Sources[d] | Total Emissions | % of Total |
Calendar Year	Plant 1	Plant 2/3[a]	Plant 4	Plant 5	Plant 6	Plant 7	Plant 8	Plant 9	Pilot Plant	Total					
1951	-	-	-	-	-	-	-	-	123	123.0	-		2	125.0	0.1
1952	-	-	-	-	6	-	-	-	493	499.0	-		44	543.0	0.3
1953	3.8	6	1473	90	12	-	-	-	493	2077.8	-		105	2182.8	1.2
1954	46.2	281	5890	4119	28	4261	201	0	271	15097.2	217	15	157	15486.2	8.7
1955	46.2	1113	12450	10410	53	7268	877	0	443	32660.2	948	118	167	33893.2	19.0
1956	43.4	1978	5145	3501	27	1743	1316	0	32	13785.4	1442	118	174	15519.4	8.7
1957	49.4	3730	814	3664.4	35	-	791	0.4	18	9102.2	1575	118	230	11025.2	6.2
1958	407.4	3520	661	715	161	-	875	679	27	7045.4	1650	118	242	9055.4	5.1
1959	46	3929	1428	478.4	127	-	260	417	34	6719.4	2100	118	240	9177.4	5.2
1960	20	4233	212	202.8	268	-	298	219	718	6170.8	2604	118	260	9152.8	5.1
1961	52.8	3707	262	76.2	119	-	209	67.4	174	4667.4	2371	118	271	7427.4	4.2
1962	14	2137	703	356	59	-	618	135	174	4196.0	2304	138	304	6942.0	3.9
1963	82.6	0	1469	783	181	-	994	159	51.8	3720.4	2171	145	339	6375.4	3.6
1964	18	0	545	330.4	34	-	1051	252	13	2243.4	2865	145	330	5583.4	3.1
1965	4.1	192.7	334.7	226.5	42.6	-	390	68	10	1268.6	5810	146.2	269	7493.8	4.2
1966	12.2	514	227.7	76.7	11.3	-	327	48.5	1213[e]	2430.4	926	152	222	3730.5	2.1
1967	20.4	646.8	279.9	147.9	2.7	-	417	76.2	11.8	1602.7	1790	152	181	3725.7	2.1
1968	0.5	1119.5	267.2	88	30.4	-	901	121.0	3.6	2531.2	3082	152	120	5885.2	3.3
1969	27.2	698.2	49.4	119.3	2.7	-	424	12.7	3.6	1337.1	3123	128	120	4708.1	2.6
1970	4.5	356.7	29.9	53.1	0	-	569	13.6	0	1026.8	666	105	185	1982.8	1.1
1971	9	306	0	0	0	-	91	0	0	406.0	541	105	40	1092.0	0.6
1972	28.4	1360	9	33	0	-	5	24	0	1459.4	-	105	37	1601.4	0.9
1973	1	1396	57	79	0	-	14	15	0	1562.0	39	105	33	1739.0	1.0
1974	1.4	2445	24.4	40	0	-	11	38	0	2559.8	-	105	32	2696.8	1.5
1975	5.6	2844.7	119.8	19	0	-	3.5	0.	0.4	2993.0	-	105	40	3138.0	1.8
1976	2.7	3339.2	26.1	13.7	2.4	-	7.2	2.8	0	3394.1	-	105	40	3539.1	2.0
1977	0.6	756.2	11.8	53.3	0	-	4.6		10.4	836.9	-	105	36	977.9	0.5
	1.8	0	11.9	29.1	0	-	0		2.2	117.0	-	105	39	261.0	(

| Calendar Year | Dust Collectors | | | | | | | | | | Plant 8 Wet Scrubbers[b] | Non-production Sources[c] | Other Sources[d] | Total Emissions | % of Total |
	Plant 1	Plant 2/3[a]	Plant 4	Plant 5	Plant 6	Plant 7	Plant 8	Plant 9	Pilot Plant	Total					
1979	0.8	0	46.3	12.3	0	-	0	2.3	0	61.7	-	93	45	199.7	0.1
1980	13.4	2.7	133.8	89.5	0	-	5.1	0	3.3	247.8	11	7.7	50	316.5	0.2
1981	1.3	30	432.1	135.6	0	-	0	0	0	599.0	10	8.2	60	677.2	0.4
1982	2.1	52.3	21	121.8	0.5	-	81.2	5.1	0	284.0	37	8.8	65	394.8	0.2
1983	6.4	130	42.9	41.4	0	-	24.7	0	0	245.4	58	7.8	65	376.2	0.2
1984	12.1	574.3	39.6	83.9	1.0	-	8.1	170.9	28	917.9	38	16.8	66	1013.5	0.6
Sub-Total	985.3	41398.3	33216.5	26189.3	1203.6	13272.0	10773.4	2598.9	4326.0	133963.3	36378.0	3086.5	4610.0	178037.8	99.4%
% of Sub-Total	0.6%	23.3%	18.7%	14.7%	0.7%	7.5%	6.1%	1.5%	2.4%	75.2%	20.4%	1.7%	2.6%	100.0%	
1985	1.1	133.9	10.2	12.4	0.0	-	4.0	2.2	6.5	170.3	24.7	-	64.0	259.0	0.1%
1986	0.0	167.0	5.6	6.7	0.0	-	2.5	1.2	3.4	186.2	105.5	-	68.0	359.7	0.2%
1987	0.0	200.0	0.9	1.0	0.0	-	0.9	0.1	0.3	203.2	32.2	-	60.0	295.4	0.2%
Sub-Total (1951-1987)	987.0	41849.2	33233.2	26209.4	1203.6	13272.0	10780.8	2602.4	4336.2	134523.6	36540.4	3086.5	5074.0[f]	179244.5[f,g]	94.9[g]
% of Sub-Total	0.6%	23.4%	18.5%	14.6%	0.7%	7.4%	6.0%	1.5%	2.4%	53.5%	20.4%	1.7%	2.8%	100.0%	
1988	0.0	66.4	2.2	1.6	0.5	-	0.6	0.2	1.2	72.7	15.6	-	17.8	126.1	0.1%
1989	0.1	0.0	0.3	0.4	0.4	-	0.3	0.2	-	1.7	3.8	-	6.9	12.1	0.0%
1990	-	-	-	-	-	-	-	-	-	0.0	-	-	1.7	1.7	0.0%
1991	-	-	-	-	-	-	-	-	-	0.0	-	-	0.2	0.3	0.0%
1992	-	-	-	-	-	-	-	-	-	0.0	-	-	0.1	0.2	0.0%
1993	-	-	-	-	-	-	-	-	-	0.0	-	-	0.2	0.2	0.0%
Total	987.1	41965.6	33235.7	26211.4	1204.5	13272.0	10781.8	2602.8	4337.4	134598.3	36559.7	3086.5	5103.4[f]	179318.5[f]	100%
% of Total	0.6%	23.4%	18.5%	14.6%	0.7%	7.4%	6.0%	1.5%	2.4%	75.1%	20.4%	1.7%	2.8%	100%

[a]Includes emissions from gulping of uranium trioxide.
[b]Data are on a fiscal year basis: 1952-1976 July 1 - June 30; 1976 transition and; 1977 and after, October 1 - September 30
[c]Consists of:
    Old solid waste incinerator (1954-1979)   2474.7 kg
    Old burner (1962-1979)   462.9 kg

Graphite burner (1965-1984)	124.6	kg
New solid waste incinerator (1980-1984)	<20	kg
Liquid organic waste incinerator (1983-1984)	<20	kg
	3086.5	kg

[d]Includes other process emissions, buildings exhausts, laboratory emissions, fugitive emissions from waste pits, and nonroutine events.

[e]Includes 1195 kg unmonitored release of UF_6 on February 14, 1966.

[f]Includes an additional 272 kg from nonroutine events not distributed over production years (concentrated liquid uranyl nitrate hexahydrate releases).

[g]Some totals differ from other published reports but differences are insignificant

Sources: 1951-1987 (Boback et al. 1987 "History of FMPC Radiological Discharges," FMPC-2082 prepared for DOE, Oak Ridge Operations Office, Oak Ridge, TN. Clark, et al. 1989, "History of FMPC Radionuclide Discharges - Revised Estimates of Uranium and Thorium Air Emissions from 1951-1987," Addendum to FMPC-2082, prepared for DOE, Oak Ridge Operations Office, Oak Ridge, TN.

1988-1993 (DOE Radioactive Effluent Information System/On-Site Discharge Information System Data Reports, 1989-1994)

TABLE F.3.I.2-3

ESTIMATE OF FORM OF URANIUM STACK DISCHARGES BY DECADE (Kg)

Plant	Species[a]	1950s	1960s	1970s	1980s	Species Total	Plant Total
1	ORES	642	149	0	0	791	
	U_3O_8	0	103	57	34	194	985
2/3	ORES	1788	414	597	0	2799	
	U_3O_8	199	45	105	6	355	
	UO_8	0	0	62	3	65	3219
4	UO_3	0	75	0	8	83	
	U_3O_8	21,349	3468	29	18	24,864	
	UF_4	6382	791	301	631	8105	
	UO_2F_2	130	16	6	13	165	33,217
5	U_3O_8	22,185	2230	322	436	25,173	
	UF_4	777	176	10	36	999	
	UO_2F_2	16	0	0	0	16	26,188
6	U_3O_8	449	751	2	2	1204	1204
7	UF_4	13,272	0	0	0	13,272	13,272
8	U_3O_8	4089	5239	706	119	10,153	
	UAP	222	371	0	0	593	
	UCl_4	9	19	0	0	28	10,774
9	U_3O_8	672	696	168	176	1712	
	UF_4	416	371	0	0	874	
	UO_2F_2	8	5	0	0	13	2599
Pilot	U_3O_8	1912	1064	13	5	2994	
	UF_4	22	115	0	1	138	3132
Total		74,537	16,187	2378	1488	94.590	

[a] U_3O_8 = uranium oxide
UO_3 = uranium trioxide
UF_4 = uranium tetrafluoride
UO_2F_2 = uranium fluoride
UAP = uranyl ammonium phosphate
UCl_4 = uranium tetrachloride

TABLE F.3.1.2-4

FEMP AIRBORNE EMISSIONS SUMMARY IN KILOGRAMS

Year	1 Uranium FMPC-2082 Totals	2 Uranium Gulping Emissions	3 Other Uranium Process Emissions	4 Uranium Emissions Building Exhausts	5 Uranium Estimated Laboratory Emissions	6 Uranium Fugitive Emissions Waste Pits	7 Uranium Emissions Nonroutine Events	8 Total Uranium Emissions*
1951	123.0	0	0	0	2	0	0	125
1952	499.0	0	0	0	2	0	42	543
1953	2077.8	0	3	1	2	0	99	2183
1954	15,119.2	210	8	5	2	0	142	15,486
1955	32,976.2	750	11	11	2	1	142	33,893
1956	13,595.4	1750	12	1	2	2	142	15,519
1957	8045.2	2750	12	26	2	48	142	11,025
1958	5513.4	3300	14	31	2	95	100	^^55
'59	5127.4	3810	15	28	2	95	100	
1960	4872.8	4020	17	33	2	108	100	9153
1961	3516.4	3640	18	30	2	121	100	7427
1962	4568.0	2070	19	26	2	125	132	6952
1963	6036.4	0	19	25	2	125	168	6375
1964	5253.4	0	22	20	2	129	157	'33
1965	7044.8	180	22	19	2	71	155	7494
1966	3048.5	460	12	16	2	49	143	3731
1967	2924.7	620	11	16	2	11	141	3726
1968	4655.2	1110	7	14	2	12	85	5885
1969	3898.1	690	7	8	2	15	88	4708
1970	487.8	310	6	6	2	16	155	1983

Year	1 Uranium FMPC-2082 Totals	2 Uranium Gulping Emissions	3 Other Uranium Process Emissions	4 Uranium Emissions Building Exhausts	5 Uranium Estimated Laboratory Emissions	6 Uranium Fugitive Emissions Waste Pits	7 Uranium Emissions Nonroutine Events	8 Total Uranium Emissions*
1971	772.0	280	5	2	2	16	15	1092
1972	614.4	950	4	3	2	15	13	1601
1973	496.0	1210	5	3	2	15	8	1739
1974	234.8	2430	4	6	2	14	6	2697
1975	318.0	2780	4	7	2	18	9	3138
1976	169.1	3330	5	7	2	20	6	3539
1977	191.9	750	5	2	2	20	7	978
1978	222.0	0	4	2	2	22	9	261
1979	154.7	0	4	1	2	31	7	200
1980	266.5	0	4	2	2	34	8	317
1981	587.2	30	5	2	2	42	9	677
1982	279.8	50	6	2	2	41	14	395
1983	181.2	130	6	4	2	40	13	376
1984	377.5	570	6	5	2	40	13	1014
Total	135,473.6	38,179	319	379	68	1371	2780**	
						Total Uranium		179,058 kg

NOTE: Numbers may not add due to round-off.
*The 1985, 1986 and 1987 emissions as reported in the Environmental Monitoring Annual Reports have been added into the column total.
**Includes 272 kg U from estimated emissions not distributed over production years.

F.3.1.3.0 GEOCHEMICAL PROCESSES INFLUENCING THE URANIUM DISTRIBUTION

F.3.1.3.1 RAINWATER/SOIL CHEMISTRY

Rainwater falling on soil media will react with minerals/solids and organic material to form porewater. The geochemistry of porewater is controlled by the pH of the rainwater, activity of carbon dioxide (CO_2) in the water/soil system, and the solubility of various minerals or leaching of solids in the soil. A mineralogical summary of FEMP soils is provided in Table F.3.1.3-1. At the FEMP site, the moderately low pH of the rainwater (about 5) is raised by dissolution reactions with carbonate mineral fragments (dolomite and calcite) present in the soil. Rainwater dissolution reactions are most likely to occur in the upper few feet of the glacial overburden, and these reactions affect the leaching of uranium from near-surface sources. The pH of the water/soil system will be buffered in the range of 7 to 8 by carbonate mineral (e.g., $CaCO_3$) dissolution, CO_2 dissolution, and carbonic acid (H_2CO_3) dissociation. Important reactions in this system are:

(1) $CaCO_3 + H_2O <-> Ca^{+2} + HCO_3^- + OH^-$

(2) $CO_2 + H_2O <-> H_2CO_3$

(3) $H_2CO_3 <-> H^+ + HCO_3^-$

The dissolution of $CaCO_3$ in water (Reaction 1) contacting air containing about 0.03 percent CO_2 results in an equilibrium pH of about 8. Lower pH values are generally observed in FEMP because the activity of CO_2 (i.e., partial pressure of CO_2) in the soil is greater than in the air, due to decomposition of organic debris and respiration of microorganisms. The higher CO_2 activity in soil drives Reaction 2 to the right to produce more H_2CO_3, which dissociates immediately (Reaction 3) to release H^+ and lower the pH. The large reservoir of carbonate minerals (30 to 50 percent of the soil) and biogenic sources of CO_2 allow the water/soil system to be buffered between 7 and 8 by the interplay of the above three reactions.

Silicate minerals present in the soil (e.g. quartz, feldspar, and clay minerals) have less influence on the chemistry of the porewater due to their low solubilities (relative to carbonate minerals) at near neutral pH values. These minerals provide silica, potassium, sodium, aluminum, and various trace metals to the porewater via dissolution and ion-exchange reactions. The weathered surface area of these minerals plays an important part in the adsorption of ions from the porewater.

F.3.1.3.2 LEACHING OF URANIUM SOLIDS

299   Uranium solids present in near-surface sources will be leached by rainwater to form a portion of the dissolved constituents (i.e., solute) delivered to the porewater. Leaching refers to removing constituents from the solid by desorption, ion exchange, and dissolution reactions. In this sense, dissolution of a solid is a subset of leaching. The extent and time (kinetics) of dissolution are primarily functions of temperature, surface area, and bond type (e.g., ionic, covalent, etc.,) in the mineral structure. The extent of mineral dissolution is expressed mathematically by the solubility product, and solubility products have been tabulated for a large number of minerals as a function of temperature. However, the time required to dissolve a given mineral to its solubility concentration is dependent on both temperature and mineral surface area. The surface area of a soil mineral is highly variable from soil to soil and this mineral commonly has an alteration rind, which precludes the use of results generated from laboratory studies on dissolution rates of unweathered minerals. What can be said in qualitative terms is that at ambient surface and subsurface temperatures, solids formed by ionic bonding (e.g., UF_4) will dissolve and approach their equilibrium concentrations on the order of days to months, whereas solids with covalent bonds (e.g., U_3O_8) may take months to years to approach their solubility concentrations. To illustrate the extent of dissolution, consider the solubility of the two most common uranium species released from past FEMP operations (U_3O_8 and UF_4, Section F.3.1.2.2.2.1) in rainwater of pH 5 at 25°C with an oxygen partial pressure of 1×10^{-30} atmospheres (corresponding to an Eh of 0.5 volts at pH 5; Brookins 1987). The reactions are:

$$(4) \quad U_3O_8 + \tfrac{1}{2}O_2 + 6H^+ <=> 3UO_2^{+2} + 3H_2O$$

$$(5) \quad UF_4 + \tfrac{1}{2}O_2 + H_2O <=> UO_2^{+2} + 2H^+ + 4F^-$$

Using the equilibrium constants reported in the EQ3/6 thermodynamic database (Version 7.2, Wolery 1992; Wolery and Daveler 1992) for the above reactions, U_3O_8 will dissolve to yield 0.14 milligrams of uranium per kilogram of water (mg U/kg water) and dissolution of UF_4 yields 42 mg U/kg water. Therefore, the solubility of UF_4 under these conditions (i.e., pH = 5, Eh = 0.5 volts, and UO_2^{+2} is the only uranium species formed) is 300 times greater than U_3O_8. It is important to highlight that the calculation above assumes UO_2^{+2} is the only uranium species formed. In natural groundwater systems, a variety of common ions (e.g., CO_3^{-2}) are available to complex UO_2^{+2}, resulting in increased dissolution of uranium solids. Most of these complexing ions are provided by dissolution reactions between rainwater and soil minerals. This important point is discussed in more detail below.

299 The solubility calculation above predicts that U_3O_8 will remain in the environment much longer than UF_4 if the particle size and emitted quantities (i.e., moles) are similar for each uranium form. As the dissolution rate of a solid is a function of the particle surface area, leaching of very fine U_3O_8 particles can yield uranium concentrations that are similar to those derived from leaching of coarser UF_4 particles — if the leaching time period is less than that required to establish solubility equilibrium. From the example above, note that if the water is allowed to equilibrate with the solids the uranium yield would be 6 orders of magnitude greater for the UF_4 relative to U_3O_8, regardless of particle size.
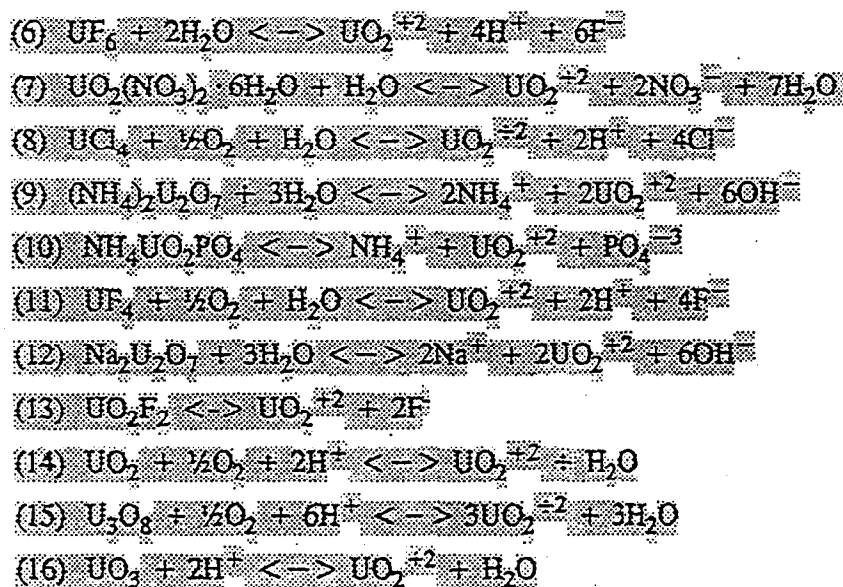
299 Another point to emphasize from the kinetic perspective is that the instantaneous release of uranium to the glacial till is tied to the rate of dissolution. Particles of UF_4 are likely to release more dissolved uranium to the glacial till than U_3O_8 particles during any given storm event (i.e., the rate of dissolution for UF_4 is greater than U_3O_8), if the mass (i.e., moles) and particle size of each form are similar. Evidence for the greater stability and persistence of uranium oxide particles in the environment (relative to uranium fluoride salts) can be gathered from the literature on uranium ore deposits. There are abundant ore deposits containing various uranium oxide minerals (Nash et al. 1981), but no reported occurrences of uranium fluoride deposits. Additionally, support for rapid dissolution and equilibration of soluble uranium salts can be found in the ORNL study on the solubility measurements of uranium in FEMP contaminated soils (Lee et al. 1993). In this study, two soils were leached to establish uranium solubility concentrations - one soil was obtained from the production area where soluble uranium is present and the other was obtained from the incinerator area where only uranium oxide particles have been released. The production area soil attained a steady uranium concentration of about 10 mg/L within a year, while the incinerator soil continued to increase its uranium concentration through 400 days (U = 4 mg/kg at 400 days). This study and research on uranium ore deposits imply that little, if any, of the UF_4 released from FEMP operations remains in the soil today. However, secondary uranium phases derived from spills of soluble uranium salts may persist in the production area. These secondary phases have moderate solubilities and their importance to the fate and transport of uranium is discussed in Section F.3.1.4.0

The use of solubility calculations can be extended to all uranium forms believed to have been released from FEMP sources (Section F.3.1.2.0) to develop a leaching hierarchy for uranium minerals. A relative ranking of mineral solubility in rainwater was obtained by computing the saturation indicies for most FEMP uranium minerals of interest. The saturation index (SI) is equal to the log of the ion

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activity product (iap) minus the log of the solubility product (sp), or SI = log(iap/sp). An SI value of zero (iap = sp) indicates the mineral is saturated in the solution (i.e., the mineral is at its solubility limit). When SI values are compared among the uranium minerals, minerals with the lowest SI values are most soluble and those with the highest values are least soluble. SI calculations were carried out with the EQ3/6 geochemical computer code (Version 7.2; Wolery 1992; Wolery and Daveler 1992) and results are summarized in Table F.3.I.3-2; results are listed in qualitative categories of most leachable (i.e., most soluble), moderately leachable, and least leachable.

299 Important dissolution reactions for uranium minerals in past and present near-surface sources (Table F.3.I.3-2) are given below:

$$(6) \quad UF_6 + 2H_2O <-> UO_2^{+2} + 4H^+ + 6F^-$$

$$(7) \quad UO_2(NO_3)_2 \cdot 6H_2O + H_2O <-> UO_2^{+2} + 2NO_3^- + 7H_2O$$

$$(8) \quad UCl_4 + \tfrac{1}{2}O_2 + H_2O <-> UO_2^{+2} + 2H^+ + 4Cl^-$$

$$(9) \quad (NH_4)_2U_2O_7 + 3H_2O <-> 2NH_4^+ + 2UO_2^{+2} + 6OH^-$$

$$(10) \quad NH_4UO_2PO_4 <-> NH_4^+ + UO_2^{+2} + PO_4^{-3}$$

$$(11) \quad UF_4 + \tfrac{1}{2}O_2 + H_2O <-> UO_2^{+2} + 2H^+ + 4F^-$$

$$(12) \quad Na_2U_2O_7 + 3H_2O <-> 2Na^+ + 2UO_2^{+2} + 6OH^-$$

$$(13) \quad UO_2F_2 <-> UO_2^{+2} + 2F^-$$

$$(14) \quad UO_2 + \tfrac{1}{2}O_2 + 2H^+ <-> UO_2^{+2} + H_2O$$

$$(15) \quad U_3O_8 + \tfrac{1}{2}O_2 + 6H^+ <-> 3UO_2^{+2} + 3H_2O$$

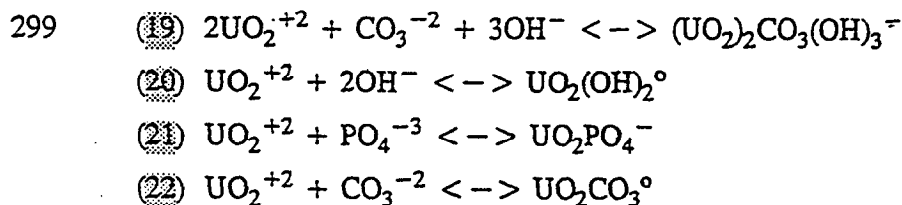$$(16) \quad UO_3 + 2H^+ <-> UO_2^{+2} + H_2O$$

299 As Reactions 6 through 13 involve uranium salts of moderate to high solubility (Table F.3.I.3-2), rainwater contacting these solids would result in rapid dissolution and subsequent mobilization of uranium. Because of their soluble nature, the uranium salts in Reactions 6 through 13 are not expected to be present in near-surface sources today due to the high annual rainfall (greater than 40 inches) and the cessation of production activities at the FEMP in 1989.

Under the wet and oxidizing surface soil conditions present at the FEMP, uranium will be leached from near-surface sources and released initially as the uranyl ion (UO_2^{+2}). UO_2^{+2} readily forms aqueous complexes with carbonate (CO_3^{-2}), phosphate (PO_4^{-3}), and hydroxide (OH^-) ions present in porewater and groundwater. The rainwater/soil reactions discussed above produce porewater and

groundwater compositions that reflect equilibrium with carbonate minerals, resulting in waters composed primarily of the ions Ca^{+2}, HCO_3^-, Mg^{+2}, and CO_3^{-2}. The CO_3^{-2} ion has a strong affinity for UO_2^{+2} and readily forms aqueous uranium complexes as follows:

299   (17) $UO_2^{+2} + 2CO_3^- <-> UO_2(CO_3)_2^{-2}$

299   (18) $UO_2^{+2} + 3CO_3^- <-> UO_2(CO_3)_3^{-4}$
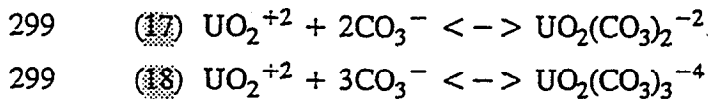
Other uranium species that are predicted (based on EQ3/6 geochemical modeling) to exist in FEMP perched groundwater at much lower concentrations are indicated below:

299   (19) $2UO_2^{+2} + CO_3^{-2} + 3OH^- <-> (UO_2)_2CO_3(OH)_3^-$

         (20) $UO_2^{+2} + 2OH^- <-> UO_2(OH)_2^\circ$

         (21) $UO_2^{+2} + PO_4^{-3} <-> UO_2PO_4^-$

         (22) $UO_2^{+2} + CO_3^{-2} <-> UO_2CO_3^\circ$

299 The formation of uranium complexes in FEMP porewater and perched groundwater enhances the dissolution of uranium minerals by decreasing the activity (i.e., concentration) of UO_2^{+2} in the water. As the UO_2^{+2} activity is lowered in Reactions 17 through 22 by the formation of the indicated complexes, the affinity to drive Reactions 6 through 16 to the right is increased, resulting in dissolution of additional uranium solids. The principle illustrated here is that formation of aqueous uranium complexes increases the uranium concentration in solution.

299 Another important observation is that the predicted uranium speciation in perched groundwater (Reactions 17 through 22) is dominated by negatively charged complexes, which have greater mobility in most water/soil systems. Most water/soil systems are dominated by particles that have a net negative charge on their surface, creating favorable conditions for the adsorption of positively charged ions (e.g., Cd^{+2}, Ra^{+2}, etc.). The adsorption of negatively charged species is controlled largely by the presence of iron, manganese, and aluminum oxyhydroxide coatings on weathered mineral grains.

298 **F.3.1.3.3 Oxidation-Reduction Reactions**

Oxidation-reduction reactions involve the transfer of electrons from one element to another. The ability of any soil, groundwater, or other natural environment to carry out an oxidation or reduction process is measured by a quantity called its redox potential or Eh. Eh measurements give insight on

the ability of an environment to supply electrons to an oxidizing agent (reducing environment) or to obtain electrons from a reducing agent (oxidizing environment). For example, uranium metal (a reducing agent) placed in the presence of rainwater at pH = 5 and Eh = 500 millivolts (mV) will give up electrons to the rainwater as the metal is transformed into $UO_3 \cdot 2H_2O$ (schoepite). The transformation occurs in a number of steps that involve the release of electrons from the metal and the use of the electrons by oxygen to form intermediate uranium oxides and eventually schoepite. A simplified redox scenario for this transformation is given in the following reactions:

$$(23)\ U \iff U^{+4} + 4e^-$$

$$(24)\ U^{+4} + 4e^- + O_2 \iff UO_2$$

$$(25)\ UO_2 \iff UO_2^{+2} + 2e^-$$

$$(26)\ UO_2^{+2} + 2e^- + \tfrac{1}{2}O_2 + 2H_2O \iff UO_3 \cdot 2H_2O$$

298 In Reaction 23, four electrons are obtained from the uranium as it it tranformed into the aqueous specie U^{+4}. The products from Reaction 23 are reacted with oxygen in Reaction 24 to form the intermediate amorphous oxide UO_2. Further oxidation of UO_2 produces the uranyl ion and two electrons (Reaction 25) which react with oxygen and water in Reaction 26 to form the final product $UO_3 \cdot 2H_2O$. The above redox example consists of two oxidation steps, however, uranium may occur in several oxidation states in the environment and numerous other oxidation-reduction reactions probably take place in the transformation of uranium metal to schoepite.

298 Uranium has three common oxidation states (+4, +5, +6) in aqueous environments, designated as U(IV), U(V), and U(VI). Important aqueous oxidation-reduction reactions between these three uranium oxidation states are:

$$(27)\ U^{+4} + 2H_2O \iff UO_2^+ + 4H^+ + e^-$$
$$(28)\ U^{+4} + 2H_2O \iff UO_2^{+2} + 4H^+ + 2e^-$$
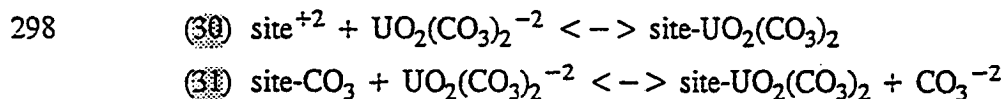$$(29)\ UO_2^+ \iff UO_2^{+2} + e^-$$

298 In the above reactions, U(IV) is oxidized to U(V) (Reaction 27) or U(VI) (Reaction 28) and U(V) is oxidized to U(VI) (Reaction 29). In glacial overburden background groundwaters having pH of 6.9 to 7.7, the dominant oxidation state is U(VI) when Eh is greater than 50 mV and U(IV) when Eh is less than 50 mV. The U(V) oxidation state is somewhat unstable with respect to the U(VI) and U(IV)

states, and U(V) does not readily occur as the dominant oxidation state in aqueous environments (Brookins 1987). When uranium is in the U(VI) state, it is readily transported as the aqueous uranyl ion (UO_2^{+2}). However, under reducing conditions favorable to the U(IV) oxidation state, uranium is stabilized as the nearly insoluble UO_2 solid. Therefore, uranium is essentially immobile in aqueous environments under reducing conditions (i.e., Eh less than zero).

298 At the FEMP, Eh measurements at four monitoring wells in the glacial overburden (Wells 1012, 1058, 1059, and 1124) ranged from 84 to 485 mV, over a pH range of 6.9 to 7.7. These Eh values correspond to an environment that is transitional between oxidizing and reducing (84 mV) to oxidizing (485 mV). The measured Eh values indicate an aqueous environment that favors the U(VI) oxidation state and, therefore, uranium is expected to be mobile in the glacial overburden. Moreover, as shown in Reactions 17 and 18, uranium mobility is enhanced further when the uranyl ion forms anion complexes with carbonate ion. The speciation and solubility of uranium in glacial overburden groundwaters of variable pH, Eh, and composition are discussed further in Section F.3.1.3.5.

298 F.3.1.3.4 ADSORPTION AND ION-EXCHANGE REACTIONS

As the redox potential of glacial overburden groundwater and the speciation of uranium into carbonate complexes enhances the solubility of uranium solids, it is unlikely that precipitation of uranium solids from perched groundwater ($HCO_3^- = 470$ mg/L) will occur at observed uranium concentrations below about 1 mg/L (as discussed in Section F.3.1.3.5). Therefore, the most important processes affecting the migration of uranium in glacial overburden media are adsorption and ion-exchange reactions with the surfaces of soil particles. Examples of these reactions for $UO_2(CO_3)_2^{-2}$ are given below:

298   (30) $site^{+2} + UO_2(CO_3)_2^{-2} <-> site-UO_2(CO_3)_2$
        (31) $site-CO_3 + UO_2(CO_3)_2^{-2} <-> site-UO_2(CO_3)_2 + CO_3^{-2}$

322 Adsorption (Reaction 31) refers to two distinct processes: physical adsorption and chemisorption
298 (Lasaga 1981). Physical adsorption results from the intermolecular or van der Waal's forces acting between the particle surface and ion. This is the initial step in removing the ion from solution. Chemisorption involves the formation of chemical or ionic bonds between the surface atoms and the adsorbed species. Although physical adsorption occurs rapidly, chemisorption is slow and requires that the physically adsorbed specie "age" on the site to allow time for the bonding reaction to take

place. Once chemisorption has occurred, it is very difficult to desorb the specie from the solid. Therefore, adsorption/desorption reactions become irreversible with time (i.e., only a fraction of what is initially adsorbed to the solid can be removed or extracted by desorption), which is in contrast to the fully reversible assumption invoked in fate and transport models by the use of the solid/liquid partition coefficient (i.e., K_d). Evidence for the irreversible nature of adsorption on the time frame of several decades is provided by adsorption and desorption batch tests with FEMP soil. The test results show mean values of 24 L/kg for adsorption and 270 L/kg for desorption. These studies and the use of adsorption and desorption values in fate and transport modeling, via the K_d approach, is discussed in Section F.3.I.5.0.

298 Ion exchange (Reaction 31) is physical adsorption that is accompanied by desorption of a different specie. The exchangeability of an adsorbed ion depends on how it is attached to the soil particle; i.e., physical adsorption versus chemisorption. Species physically adsorbed to the soil particle surface are readily exchanged, while chemisorbed particles are more commonly exchanged only when they are on the corners or edges of particle fragments. In this paper, the term adsorption is used in a generic sense to include all processes in the continuum of physical adsorption, chemisorption, and ion exchange.

Adsorption of negatively charged uranyl carbonate species can take place on mineral surfaces that have a pH zero point of charge (pH_{zpc}) above the water/soil system pH. The pH_{zpc} is the pH at which the net charge on a mineral's surface is zero. When the pH of the water/soil system is below the mineral's pH_{zpc}, there is a net positive charge on its surface and the mineral has an affinity for negatively charged species. At the FEMP, the pH of perched groundwaters is generally near 7.5. Therefore, minerals with a pH_{zpc} above 7.5 will contain potential adsorption sites for negatively charged uranyl carbonate species. Minerals present in the glacial overburden that fit this description are summarized in Table F.3.I.3-3, along with the pH_{zpc} reported by Stumm and Morgan (1981) for oxide and hydroxide minerals and values calculated by the EQ3/6 geochemical code for calcite and dolomite.

323 The most important oxide and hydroxide surfaces are found on minerals containing aluminum and iron (Table F.3.I.3-3). Weathering of feldspar and amphibole minerals (Table F.3.I.3-1) to clay minerals can produce the oxide and hydroxide phases noted in Table F.3.I.3-3. Additionally, clay minerals (illite, corrensite, chlorite, and iron oxyhdroxide minerals in Table F.3.I.3-1) can provide

the aluminum and iron oxyhydroxide surfaces to catalyze the adsorption reactions. A discussion on the mass of uranium available for sorption reactions will be presented as part of the Operable Unit 5 FS Report in November, 1994.

323   For the carbonate minerals present in the glacial overburden (Table F.3.I.3-1), the pH_{zpc} is dependent on the partial pressure of CO_2 (Table F.3.I.3-3). Rainwater equilibrated with air ($P_{CO2} = 10^{-3.5}$) has a lower CO_2 partial pressure than soil containing organic material and microorganisms. Measurements of the composition of gas samples from soil generally show CO_2 partial pressures from 10^{-3} to 10^{-1} (Freeze and Cherry 1979). The higher CO_2 partial pressure in soil atmosphere drives Reaction 2 to the right to produce more H_2CO_3. Dissociation of the additional H_2CO_3 leads to higher concentrations of HCO_3^- and H^+, which lowers a carbonate minerals pH_{zpc} (Stumm and Morgan 1981). In Table F.3.I.3-3, the pH_{zpc} for calcite drops from 8.4 to 7.6 as P_{CO2} is raised from $10^{-3.5}$ to $10^{-2.5}$. This implies that the carbonate minerals in the glacial overburden will not be very efficient at adsorption of uranyl carbonate species, and this is reflected in the low adsorption values selected for the fate and transport model. Specific adsorption values used to model uranium migration in the glacial overburden are discussed in Section F.3.1.5.0.

298   F.3.I.3.5   <u>URANIUM MINERAL SOLUBILITY IN PERCHED GROUNDWATER</u>

325   The concentration of uranium in glacial overburden groundwater will be controlled by the dissolution rates of uranium solids in the soil, the adsorption of uranium onto glacial till solids, the solubility of uranium minerals in perched groundwater, and hydraulic factors such as flow rates, flow volumes, and residence times (hydraulic factors are discussed in detail in Section 3.6). Observed uranium concentrations in glacial overburden groundwater at the FEMP range from 0.00029 to 129 mg/L (Table E.1-1). Using groundwater constituent concentrations for Monitoring Wells 1060 (pH 7.67) and 1065 (pH 6.97) (Appendix I) and a uranium concentration of 129 mg/L, mineral SIs were calculated at Eh values of 84 and 485 mV to evaluate the saturation state of uranium phases over the range of pH and Eh conditions found in glacial overburden groundwater (Tables F.3.I.3-4 and F.3.I.3-5).

325   In groundwater obtained from Monitoring Wells 1060 (pH = 7.67, UO_2^{+2} = 146 mg/L) and 1065 (pH = 6.97, UO_2^{+2} = 146 mg/L), nine uranium phases are predicted to be supersaturated (SI > 0.4) or saturated (0.4 > SI > -0.4) at an Eh of 84 mV, but only four phases at an Eh of 485 mV (Tables F.3.I.3-4 and F.3.I.3-5, respectively). At an Eh of 84 mV, haiweeite, soddyite, U_3O_8,

U_3O_8, U_4O_9, and uraninite are supersaturated in groundwater from both wells, $CaUO_4$ and coffinite are respectively supersaturated in groundwater from Wells 1060 and 1065, coffinite and sklodowskite are saturated in groundwater from Well 1060, and $(UO_2)_3(PO_4)_2 \cdot 4H_2O$ and schoepite are saturated in groundwater from Well 1065. Note that the SI values for minerals containing uranium in the U(VI) oxidation state do not change as a function of Eh, indicating U(VI) is the stable oxidation state over the Eh range of 84 to 485 mV. However, the uranium oxides containing uranium in the U(IV) and U(V) oxidation states are thermodynamically unstable at an Eh value of 485 mV, and their SI values decrease to less than -10 (indicating they will not precipitate in the glacial overburden under this Eh condition). However, these thermodynamic calculations do not consider dissolution kinetics, and although the U(IV) and U(V) oxidation states are thermodynamically unstable at an Eh value of 485 mV, minerals with U(IV) and U(V) that are currently present in the environment may persist for decades to thousands of years if the dissolution kinetics are slow (e.g., UO_2). Additionally, groundwater flow volumes and residence times will affect the degree to which uranium solids are dissolved. Lacking kinetic data on the dissolution rates of the uranium phases, all that can be said is that the observed uranium concentrations in glacial overburden groundwater show that residence times are great enough to achieve concentrations that can saturate a number of uranium phases.

325 It is of interest that the elements comprising the supersaturated and saturated uranium phases listed above (i.e., Si, P, Ca, Mg, O) have all been detected in uranium grains found in contaminated FEMP soil (Lee and Marsh 1992), although specific minerals could not be identified by this ORNL study because the SEM and EDX analysis did not yield stoichiometric information. However, the thermodynamic solubility calculations and ORNL elemental data suggest that the predicted saturated phases can be present in FEMP soil.

325 Assuming precipitation kinetics allow any of the supersaturated and saturated phases to form at ambient temperature over the time frame of FEMP operations (e.g., decades), it is useful to identify the minimum uranium concentration required to precipitate a given mineral (i.e., the uranium concentration that will set a mineral SI equal to zero). These concentrations have been calculated for the supersaturated and saturated phases in Tables F.3.13-4 and F.3.13-5 at an Eh of 84 mV (Table F.3.13-6). Note that the presented concentrations cover the range of observed uranium concentrations in glacial overburden groundwaters, indicating groundwater residence times are great enough to achieve saturation with respect to the indicated phases.

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325 For the uranium minerals in Table F.3.1.3-6 containing the U(IV) and U(V) oxidation states (β-U_3O_7, U_3O_8, U_4O_9, UO_2, and $USiO_4$) higher uranium concentrations are required to saturate these phases in groundwater from Well 1060. This is primarily due to a partial pressure of oxygen (P_{O2}) that is about three orders of magnitude higher in groundwater from Well 1060. Higher P_{O2} destabilizes the U(IV) and U(V) oxidation states, which increases the solubility of the indicated minerals. The higher P_{O2} in groundwater from Well 1060, relative to Well 1065, is due to a higher pH value - as P_{O2} is a function of pH at constant Eh (i.e., 84 mV). Variation in the uranium concentrations required to saturate minerals containing uranium in the U(VI) oxidation state is largely due to the difference in pH and element concentrations (e.g., Ca, P, Si, Mg) in the groundwater from the two wells. Although any one or several of the phases in Table F.3.1.3-6 may precipitate from either groundwater when the observed maximum uranium concentration has the lowest observed Eh value, it is important to note that the minerals containing U(IV) and U(V) will not precipitate when the P_{O2} exceeds 10^{-44} atmospheres (about 200 mV at pH 6.97). Therefore, under most Eh and pH conditions measured in glacial overburden groundwater, the precipitation of secondary uranium phases is expected to be limited to minerals containing the U(VI) oxidation state.

It is important to emphasize that mineral solubility is only one of several geochemical processes that may control uranium concentrations in perched groundwater. Table F.3.1.3-6 indicates that uranium concentrations in groundwater have to be on the order of 0.2 mg/L (at pH = 6.97, Eh = 84 V) the least soluable uranium phase will precipitate. Therefore, if the soluble uranium phases in the source have been removed by leaching, future uranium concentrations in groundwater may never reach saturation with respect to the other uranium solids. Under this future scenario, the uranium concentration in perched groundwater will be controlled by dissolution rates in the source and adsorption reactions in the soil. This scenario is hypothesized to be the most probable case for present sources of uranium oxide particles derived from air emissions, while mineral solubility may control some uranium concentrations observed in present groundwater contaminated by past spills of uranyl nitrate and other uranium solutions.

298 F.3.1.3.6 SUMMARY

Uranium will be mobilized in source areas by rainwater leach. and aqueous complexation of the uranyl ion with carbonate ion. Leaching in the source takes place by dissolution of uranium solids and desorption of uranium from soil particles. As the mobilized uranium migrates away from the source, the plume encounters lower portions of the glacial overburden where adsorption of uranium

and/or precipitation of uranium may occur. Precipitation of uranium will be controlled primarily by the concentration of carbonate ion, with waters having higher aqueous carbonate concentrations suppressing uranium precipitation by formation of uranyl carbonate complexes.

326 Finally, it is important to highlight the contrast between the heterogeneous uranium forms in the source area and the homogeneous uranium forms in the water/glacial overburden system. The heterogeneity of uranium forms in the different source areas results in a wide range of release concentrations to porewater and groundwater (Table F.3.1.3-2 and Reactions 6 through 14). However, once the uranium has been released to the porewater and groundwater, the uranium is homogenized throughout the FEMP area as uranyl carbonate species (Reactions 17 and 18), with the exception of secondary uranium precipitates that may form (e.g., $CaUO_4$, $(UO_2)_3(PO_4)_2 \cdot 4H_2O$). If present, the secondary precipitates will influence the uranium groundwater concentrations at some future date, although mass balance information is not available to estimate the amount of uranium that may be tied up in these secondary precipitates. This conceptual picture is important to recall throughout the discussion presented in Sections F.3.1.4.0 and F.3.1.5.0.

TABLE F.3.I.3-1

MINERALOGICAL SUMMARY OF FEMP GLACIAL OVERBURDEN SOIL

Phase/Ideal Formula	Modal Percent[a]
Calcite $CaCO_3$	25.75 ± 11.62
Dolomite $MgCa(CO_3)_2$	20.77 ± 10.53
Quartz SiO_2	18.03 ± 8.58
Feldspar $KAlSiO_3$	14.76 ± 6.49
Illite $KAl_5Si_7O_{20}(OH)_4$	9.15 ± 17.37
Corrensite $NaCaMg_8Fe_5Al_5Si_{14}O_{40}(OH)_{20}$	4.27 ± 8.30
Organic debris (humus)	3.49 ± 3.68
Chlorite $Mg_7Fe_4Al \cdot O_{20}(OH)_{16}$	1.13 ± 1.50
Amphibole $KCa_2M \cdots e_2Al_2Si_6O_{20}(OH)_4$	0.95 ± 0.72
Iron oxyhydroxide minerals $Fe(OH)_3$, $FeOOH$, Fe_2O_3	0.83 ± 0.72

[a]Average and standard deviation of 20 soil samples analyzed by McCrone Associates, Inc. (1992). Modal percent is based on the mineral area exposed on a thin section prepared for microscopic examination.

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299   TABLE F.3.I.3-2

LEACHABILITY OF FEMP URANIUM SOLIDS IN RAINWATER AT 25°C

Most Leachable (SI[a])	Moderately Leachable (SI)	Least Leachable (SI)
UF_6 (−90.0)	UF_4 (−36.6)	UO_2 (−11.8)
$UO_2(NO_3)_2 \cdot 6H_2O$ (−78.7)	$Na_2U_2O_7$ (−20.1)	U_3O_8 (−11.1)
UCl_4 (-76.0)	UO_2F_2 (-16.1)	UO_3 (−7.43)
$NH_4UO_2PO_4$[b]		
$(NH_4)_2U_2O_7$[b]		

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[a] Saturation Index (SI) calculated with the EQ3/6 geochemical code using pH = 5, Eh = 0.5 Volts (P_{O2} = 5.1 x 10^{-30} atm), and U = 0.001 mg/L. Lowest SI values correspond to most soluble, or leachable, uranium forms.

[b] Mineral is not in EQ3/6 thermodynamic database; therefore, SI is unavailable. Ammonium salts are generally very soluble, and this assumption is used to support the placement of these minerals in the most leachable category.

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TABLE F.3.1.3-3

GLACIAL OVERBURDEN MINERALS WITH pH_{zpc} GREATER THAN 7.5^a

Mineral	pH_{zpc}
Calcite $CaCO_3$	8.4^b (7.6^c)
Dolomite $MgCa(CO3)_2$	8.3^b (7.5^c)
Aluminum oxide $\alpha-Al_2O_3$	9.1
Aluminum oxyhydroxide $\gamma-AlOOH$	8.2
Iron oxyhydroxide $\alpha-FeOOH$	7.8
Amorphous iron hydroxide $Fe(OH)_3$	8.5

[a]Oxide and hydroxide minerals compiled from Stumm and Morgan (1981).
[b]pH_{zpc} calculated with EQ3/6 geochemical code for $P_{CO2} = 10^{-3.5}$.
[c]pH_{zpc} calculated with EQ3/6 geochemical code for $P_{CO2} = 10^{-2.5}$.

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TABLE F.3.1.3-4

SATURATION INDICIES FOR URANIUM MINERALS
IN PERCHED GROUNDWATER FROM WELL 1060[a] (pH = 7.67)

Mineral Formula (name)	SI^b	
	Eh = 84 mV P_{O2} = 2.5x10^{-50} atm	Eh = 485 mV P_{O2} = 2.9x10^{-22} atm
$Ca(UO_2)_2(Si_2O_5)_3 \cdot 5H_2O$ (haiweeite)	5.417	5.417
$(UO_2)_2SiO_4 \cdot 2H_2O$ (soddyite)	5.067	5.067
β-U_3O_7	2.209	–[c]
U_3O_8	1.199	–
U_4O_9	1.134	–
UO_2 (uraninite)	0.484	–
$CaUO_4$	0.429	0.429
$USiO_4$ (coffinite)	-0.024	–
$Mg(H_3O)_2(UO_2)_2(SiO_4)_2 \cdot 4H_2O$ (sklodowskite)	-0.058	-0.058
$UO_3 \cdot 2H_2O$ (schoepite)	-0.456	-0.456
β-$UO_2(OH)_2$	-0.606	-0.606
α-$UO_3 \cdot 0.9H_2O$	-0.675	-0.675
UO_2CO_3 (rutherfordine)	-1.389	-1.389
$(UO_2)_3(PO_4)_2 \cdot 4H_2O$	-2.042	-2.042
$Mg(UO_2)_2(PO_4)_2$ (saleeite)	-2.502	-2.502
$Ca(UO_2)_2[SiO_3(OH)]_2 \cdot 5H_2O$ (uranophane)	-3.255	-3.255
γ-UO_3	-3.514	-3.514
$UO_2HPO_4 \cdot 4H_2O$	-3.631	-3.631
UO_2 (amorphous)	-3.984	–
UO_2HPO_4	-4.067	-4.067
β-UO_3	-4.138	-4.138
α-UO_3	-4.484	-4.484
$CaU(PO_4)_2 \cdot 2H_2O$ (ningyoite)	-4.670	–
UPO_5	-4.681	–
$UO_2FOH \cdot 2H_2O$	-5.003	-5.003

TABLE F.3.I.3-4
(Continued)

Mineral Formula (name)	SI[b]	
	Eh = 84 mV $P_{O2} = 2.5 \times 10^{-50}$ atm	Eh = 485 mV $P_{O2} = 2.9 \times 10^{-22}$ atm
$Na_2U_2O_7$	-5.162	-5.162
$UO_2FOH \cdot H_2O$	-5.436	-5.436
UO_2FOH	-5.936	-5.936
$UOFOH \cdot 0.5H_2O$	-7.104	—
$NaUO_3$	-7.159	—
$MgUO_4$	-7.341	-7.341
$U_5O_{12}Cl$	-7.442	—

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[a] Using average groundwater concentration for Well 1060.

[b] Saturation Index (SI) calculated with EQ3/6 geochemical code (Version 7.2) for $UO_2^{+2} = 146$ mg/L.

[c] — means SI ≤ -10.

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TABLE F.3.I.3-5

SATURATION INDICIES FOR URANIUM MINERALS
IN PERCHED GROUNDWATER FOR WELL 1065[a] (pH = 6.97)

Mineral Formula (name)	SI[b]	
	Eh = 84 mV P_{O2} = 4.4x10^{-53} atm	Eh = 485 mV P_{O2} = 5.0x10^{-25} atm
$(UO_2)_2SiO_4 \cdot 2H_2O$ (soddyite)	5.286	5.286
β-U_3O_7	4.380	—[c]
$Ca(UO_2)_2(Si_2O_5)_3 \cdot 5H_2O$ (haiweeite)	3.702	3.702
U_3O_8	2.449	-6.902
U_4O_9	2.334	—
UO_2 (uraninite)	2.029	—
$USiO_4$ (coffinite)	1.410	—
$(UO_2)_3(PO_4)_2 \cdot 4H_2O$	0.203	0.203
$UO_3 \cdot 2H_2O$ (schoepite)	-0.291	-0.291
β-$UO_2(OH)_2$	-0.441	-0.441
UO_2CO_3 (rutherfordine)	-0.516	-0.516
α-$UO_3 \cdot 0.9H_2O$	-0.510	-0.510
$CaUO_4$	-0.781	-0.781
$Mg(H_3O)_2(UO_2)_2(SiO_4)_2 \cdot 4H_2O$ (sklodowskite)	-1.306	-1.306
$Mg(UO_2)_2(PO_4)_2$ (saleeite)	-1.777	-1.777
UO_2 (amorphous)	-2.439	—
$UO_2HPO_4 \cdot 4H_2O$	-2.591	-2.591
$CaU(PO_4)_2 \cdot 2H_2O$ (ningyoite)	-2.751	—
UPO_5	-2.951	—
UO_2HPO_4	-3.028	-3.028
$U_5O_{12}Cl$	-3.093	—
γ-UO_3	-3.349	-3.349
β-UO_3	-3.973	-3.973
α-UO_3	-4.319	-4.319
$UO_2FOH \cdot 2H_2O$	-4.328	-4.328

TABLE F.3.I.3-5
(Continued)

Mineral Formula (name)	SI[b]	
	Eh = 84 mV $P_{O2} = 4.4 \times 10^{-53}$ atm	Eh = 485 mV $P_{O2} = 5.0 \times 10^{-25}$ atm
$Ca(UO_2)_2[SiO_3(OH)]_2 \cdot 5H_2O$ (uranophane)	-4.524	-4.523
$UO_2FOH \cdot H_2O$	-4.761	-4.761
$UOFOH \cdot 0.5H_2O$	-5.049	--
UO_2FOH	-5.262	-5.262
$UOFOH$	-5.542	--
$H_2(UO_2)_2(PO_4)_2$ (H-autunite)	-6.252	-6.252
$UO_2SO_4 \cdot H_2O$	-6.599	-6.599
$Na_2U_2O_7$	-6.976	-6.975
$UOF_2 \cdot H_2O$	-7.222	--
$NaUO_3$	-7.376	--

[a] Using average groundwater concentration for Well 1065.
[b] Saturation Index (SI) calculated with EQ3/6 geochemical code (Version 7.2) for $UO_2^{+2} = 146$ mg/L.
[c] -- means SI $\leq$ -10.

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TABLE F.3.1.3-6

URANIUM CONCENTRATIONS REQUIRED TO SATURATE[a] SELECT URANIUM PHASES IN PERCHED GROUNDWATER FROM WELLS 1060 AND 1065

Mineral Formula (name)	Uranium Concentration (mg/L)	
	1060	1065
$(UO_2)_2SiO_4 \cdot 2H_2O$ (soddyite)	0.49	0.19
β-U_3O_7	13.4	0.53
$Ca(UO_2)_2(Si_2O_5)_3 \cdot 5H_2O$ (haiweeite)	0.32	1.16
U_3O_8	38.9	5.08
U_4O_9	12.6	0.38
UO_2 (uraninite)	51.8	0.77
$USiO_4$ (coffinite)	145	3.28
$(UO_2)_3(PO_4)_2 \cdot 4H_2O$	700	102
$UO_3 \cdot 2H_2O$ (schoepite)	349	318
$CaUO_4$	53.7	1338
$Mg(H_3O)_2(UO_2)_2(SiO_4)_2 \cdot 4H_2O$ (sklodowskite)	137	958

[a] Saturate means SI = 0 for P_{O2} = 2.5x10^{-50} atm (Eh = 84 mV) at pH = 7.67 (Well 1060), and P_{O2} = 4.4x10^{-53} atm (Eh = 84 mV) at pH = 6.97 (Well 1065).

F.3.I.4.0 DISTRIBUTION OF URANIUM IN THE GLACIAL OVERBURDEN

F.3.I.4.1 INTRODUCTION

Past releases of uranium from the FEMP occurred in two ways: spills from the handling of uranium solutions in Plants 2/3, 6, and 8 (estimated to be 1,300 kg of uranium; RAC 1994); and air emissions from the pilot plant and Plants 1, 2/3, 4, 5, and 8 (estimated to be 179,000 kg of uranium; Table F.3.I.2-2). Accidental spills resulted in concentrated, mobile point sources in the form of uranyl nitrate, ammonium uranyl, and other uranium solutions, while air emissions led to site-wide deposition of uranium fluoride and oxide solids. The leachability, and hence mobility, of uranium solids processed at the FEMP is summarized and discussed in Table F.3.I.3-2 and Section F.3.I.3.0.

Discussed in this section is the past, present, and future uranium distribution in the glacial overburden based on the uranium solids given in Table F.3.I.3-2 and the aqueous uranium forms discussed in Section F.3.I.2.0. The temporal distribution will be discussed with respect to releases in the production area (i.e., aqueous spills and air emissions) and those areas outside of the production area, Operable Units 1, 2, and 4 (i.e., air emissions only).

F.3.I.4.2 INITIAL URANIUM DISTRIBUTION AT TIME OF RELEASE

326 Figure F.3.I.4-1a is a schematic cross section of FEMP glacial overburden showing a conceptual view of the initial uranium distribution in the production area. Although the release events occurred over a 30-year period (1955 to 1985), the conceptual view in Figure F.3.I.4-1a depicts all releases as occurring simultaneously at some time in the past. In the illustrated scenario on Figure F.3.I.4-1a, aqueous acid spills released mobile forms of uranium that immediately began to percolate into and react with the glacial overburden. If uranium concentrations in the aqueous spills exceeded mineral solubilities after reactions with glacial overburden, precipitation of $(UO_2)_3(PO_4)_2 \cdot 4H_2O$, $CaUO_4$, $Mg(UO_2)_2(PO_4)_2$, $UO_3 \cdot 2H_2O$, and/or other uranium solids may have occurred (see Tables F.3.I.3-4, F.3.I.3-5 and F.3.I.3-6 in Section F.3.I.3.5). The initial distribution of solids released by air emissions is restricted to the top 18 inches of the soil.

Figure F.3.I.4-2a illustrates the initial conditions for uranium release in areas outside of the production area. In these areas, aqueous forms of uranium are absent during the initial deposition, as

uranium is deposited as particles derived from air emissions. The more soluble form of these uranium particles (e.g., UF_6) is rapidly dissolved upon the first storm event.

327 Other operable unit mass loadings and geochemical concepts related to nonairborne releases (leachate) have been accounted for in the Operable Unit 5 fate and transport model by directly including mass loading terms determined in previous RI fate and transport models. These mass loadings were simulated for 40 years in the Operable Unit 5 model and terminated as remedial actions are completed in other operable units. This approach is explained in Section 5.1.1 and F.3.4. The K-65 slurry trench was also included in the Operable Unit 5 RI (Source Area 570b).

F.3.1.4.3 URANIUM DISTRIBUTION AT THE PRESENT TIME

326 The present-day scenario under the production area is conceptualized in Figure F.3.1.4-1b, which shows uranium distributed throughout most of the glacial overburden. Soluble uranium forms have been removed by leaching, leaving the less soluble U_3O_8, UO_2, and UO_3. The primary uranium phases may be mixed with alteration products like $UO_3 \cdot 2H_2O$ and precipitates of $CaUO_4$ and $(UO_2)_3(PO_4)_2 \cdot 4H_2O$ throughout the upper portion of the brown glacial overburden. The uranium plume generated from the dissolution of soluble $UO_2(NO_3)_2 \cdot 6H_2O$, UF_6, UF_4, and $Na_2U_2O_7$ particles commingles with the plume derived from spills of aqueous uranium solutions. Principal aqueous species in the migrating plumes are predicted to be $UO_2(CO_3)_2^{-2}$ and $UO_2(CO_3)_3^{-4}$, with minor formation of $(UO_2)_2CO_3(OH)_3^{-}$, $UO_2(OH)_2^{\circ}$, and $UO_2PO_4^{-}$. Adsorption of uranium on soil particles may be accompanied by precipitation of the uranium solids listed in Table F.3.1.3-6. Site-specific data supporting this conceptual scenario are presented after discussing the uranium distribution in areas outside of the production area.

326 Figure F.3.1.4-2b summarizes the present conceptual model for uranium distribution in areas impacted solely by uranium particles derived from past atmospheric releases. The uranium plume generated from the dissolution of soluble UF_6, UF_4, and $Na_2U_2O_7$ particles has reached the lower section of the glacial overburden in some areas. Principal aqueous species in the migrating plume are predicted to be $UO_2(CO_3)_2^{-2}$ and $UO_2(CO_3)_3^{-4}$, with minor formation of $(UO_2)_2CO_3(OH)_3^{-}$, $UO_2(OH)_2^{\circ}$, and $UO_2PO_4^{-}$. Adsorption of uranium on soil particles may be accompanied by precipitation of the uranium solids listed in Table F.3.1.3-6, if a large mass of soluble uranium particles was present initially. Site-specific data supporting this conceptual scenario are presented below.

Across most of the FEMP site, the released uranium is concentrated in the upper 1.5 feet of the glacial overburden and may reach uranium concentrations of greater than 1000 mg/kg of soil (Plates D-10 through D-19; see Plates in DOE, 1994). The uranium forms in the upper 15 feet of weathered and fractured soil are expected to be dominated by the less soluble oxides U_3O_8, UO_2, and UO_3, possibly mixed with precipitates of $CaUO_4$ and $(UO_2)_3(PO_4)_2 \cdot 4H_2O$. $CaUO_4$ and $(UO_2)_3(PO_4)_2 \cdot 4H_2O$ are predicted to be present based on EQ3/6 modeling results using solution analyses obtained from a 70-day leach of surface soil contaminated with uranium oxide particles (Lee et al. 1993). Much of the uranium in the per 15 feet of the glacial overburden may have been distributed by mechanical processes after deposition. For example, air emission particles that have been reworked into the upper portion of the glacial overburden by construction activities are transported into fractures by percolating rainwater. However, neutralization of acidic uranyl nitrate spills by carbonate minerals may have produced local areas of intense uranium precipitation in the upper few feet of soil. The persistence of these areas through time is dependent on the solubility of the precipitated solid and the volume of percolating water that contacts the precipitate.

326 Analytical data collected on subsurface soil samples indicate that uranium is distributed throughout the glacial overburden to a depth of 20 feet in the general area surrounding the pilot plant, Plant 2/3, and Plants 6 and 9 (Plates D-10 through D-19). Uranium concentrations in the 15- to 20-foot interval of unfractured gray glacial till reach values greater than 100 mg/kg. The presence of uranium in this interval implies geochemical, rather than mechanical processes are responsible for the distribution. Aqueous spills, rainwater dissolution of $UO_2(NO_3)_2 \cdot 6H_2O$, UF_6, UF_4, and $Na_2U_2O_7$ particles, and reactions with carbonate minerals in the glacial overburden mobilize the uranium primarily as the aqueous species $UO_2(CO_3)_2{}^{-2}$, $UO_2(CO_3)_3{}^{-4}$, and to a lesser extent as $(UO_2)_2CO_3(OH)_3{}^-$, $UO_2(OH)_2{}^o$, and $UO_2PO_4{}^-$. Percolating rainwater transports the species into the subsurface where adsorption and possibly precipitation occur to redistribute the uranium in the subsurface soil. Solids predicted to precipitate in the subsurface include the minerals listed in Table F.3.1.3-6.

326 As noted in Section F.3.1.3.0, uranium concentrations range from 0.00029 to 129 mg/L in groundwater perched within the glacial overburden. Groundwater or porewater containing high uranium concentrations will partition some of the uranium into and onto the soil by precipitation and adsorption processes. The maximum observed uranium concentration (129 mg/L) is sufficient to saturate a number of uranium phases (Table F.3.1.3-6) in perched groundwater having high bicarbonate activity, implying some of the saturated phases may be present in the glacial overburden.

Scanning electron microscope work conducted on FEMP soil by Oak Ridge National Laboratory (ORNL) noted the association of calcium, phosphorous, silicon and magnesium with uranium particles (Lee and Marsh 1992), supporting the presence of the listed uranium phases (Table F.3.13-6) in the soil.

328 Lysimeters placed near the base of the unweathered glacial overburden recovered fluid samples with uranium concentrations that varied from 0.002 to 0.052 mg/L. The lysimeters are installed at three different locations (Figure 3-37). At each of the three locations one lysimeter is installed in the base of the gray clay and one is installed in the upper unsaturated portion of the Great Miami Aquifer, immediately below the base of the gray clay.

328 Lysimeters 11234 and 11129 are located a few hundred feet northwest of the inactive flyash pile. The lysimeter cup in 11234 is located 13.6 feet below the ground surface in approximately 10 feet of gray clay. The lysimeter cup in 11129 is located beneath 11234, approximately 21.6 feet below the ground surface, in the unsaturated portion of the Great Miami Aquifer.

328 Lysimeters 11130 and 11131 are located approximately 1000 feet southeast of the southeast corner of the east parking lot. The lysimeter cup in 11130 is located 21.5 feet below the ground surface in approximately 20 feet of gray clay. The lysimeter cup in 11131 is located beneath 11130, approximately 35.6 feet below the ground surface, in the unsaturated portion of the Great Miami Aquifer.

328 Lysimeters 11132 and 11133 are located just northeast of the northeast corner of the former production area. The lysimeter cup in 11132 is located 25.6 feet below the ground surface in approximately 30 feet of gray clay. The lysimeter cup in 11133 is located beneath 11132, approximately 47.6 feet below the ground surface, in the unsaturated portion of the Great Miami Aquifer.

330 Sampling results for the lysimeters are presented in Table 3-19; results are also discussed in Section 328 4.7. Sampling information indicates uranium mobilized on the surface of the glacial overburden is capable of infiltrating to the base of the glacial overburden in less than 40 years. Major ions in the porewater have concentrations similar to perched groundwater, but pH, silica, and phosphate measurements are unavailable. Using major ion analyses of the porewater from Boring 11133, a

uranium concentration of 0.052 mg/L, and silica and phosphate analyses from perched groundwater. mineral saturation in the pore fluid was evaluated at a pH of 7.2 (t̶ ̶ed on the pH for calcite saturation in the porewater). Results of the EQ3/6 run indicate all uranium minerals are undersaturated in the porewater. This implies that the uranium distribution in soil at the base of the unweathered glacial overburden (i.e., in excess of background) is controlled by adsorption.

F.3.I.4.4 URANIU͟͟ D ͟RIBUTIC̶ ̶T SOME FUTURE TIME

Most of the present source ̶ ̶i U$_3$O$_8$, ̶ ̶. and UO$_3 \cdot$2H$_2$O, and possibly CaUO$_4$ and (UO$_2$)$_3$(PO$_4$)$_2 \cdot$4H$_2$O, in the upper 1.5 feet of glacial overburden will be remediated through soil washing and/or removed for solidification. Therefore, the future distribution of uranium in the glacial overburden will be controlled by desc̶·̶·̶·̶n of physically adsorb̶ ̶ranium and dissolution of (UO$_2$)$_3$(PO$_4$)$_2 \cdot$4H$_2$O, Mg(UO$_2$)$_2$(PO̶.̶ ̶UO̶ ̶O$_3 \cdot$2H$_2$O, a̶ ̶.̶or other uranium particles in the subsurface. This scenario is depicted in Figures F.3.I.4-1c and F.3.I.4-2c. Semiquantification of this future uranium distribution is addressed in the remaining discussion of this section.

330   Based on a hypothetical Operable Unit 5 FS clean-up level of 50 mg U/kg soil, future uranium concentrations in subsurface soil will be less than or equal to 50 mg/kg. If the uranium is assumed to be physically adsorbed, then bounds can be placed on the future concentration of uranium in glacial overburden porewater and groundwater by using the calculated adsorption/desorption values for the 15- to 20-foot depth of glacial overburden (Wells 1348, 1354, 1360, 1266, 1317, 1341, 1225, 1230, and 1250 in Table F.3.II.3-3 of Attachment F.3.II). The lowest and highest adsorption/desorption values for the indicated well locations are 12 and 2433 L/kg, yielding respective uranium concentrations of 4.1 and 0.02 mg/L in groundwat̶.̶ ̶ :ilibrated with a soil containing 50 mg of adsorbed U/kg soil (i.e., 50 mg/kg = 12 L/kg and 50 mg/kg = 2344 L/kg). It should be noted that these predicted groundwater concentrations exceed or equal the proposed maximum concentration level (MCL) of 0.02 mg/L. However, these calculati̶.̶ ̶.̶:̶ are for illustrative purposes only and are not intended to serve as the soil or groundwater concentrations that will be evaluated in the Operable Unit 5 FS.

330   As noted in Section F.3.I.3.0, desorption of adsorb̶ ̶·̶anium will der̶-̶nd on the extent of chemisorption, with the expectation that with time ̶r̶ ̶ption values w̶:̶.̶:̶ be higher than adsorption values as uranium is retained or incorporated into t̶.̶.̶ ̶:̶id by chemisorption (which is evident in the ̶—̶ 75 to 2433 L/kg range of values reported in Table F.3.II.3-3. Therefore, a groundwater MCL of

0.02 mg/L for uranium can be achieved if the soil contains less than 50 mg of adsorbed U/kg and the
K_d for desorption is greater than 2400 L/kg.

330 For particulate uranium that remains in FEMP soil after remediation efforts are completed, useful
information can be extracted from the ORNL leaching study (Lee et al. 1993) to estimate the fraction
of uranium leached and released during a three day storm event. A conclusion from the leaching of
A-14 and B-16 soil is that 0.1 to 4.5 percent, respectively, of the available uranium may be leached
from this soil in three days of leaching (i.e., a large storm event). If FEMP soil of density 1.8 kg/L
contains 50 mg of particulate uranium per kg of soil (Operable Unit 5 hypothetical clean-up level) and
the porosity is 30 percent, 1 liter of water will contact 3.3 liters of soil — or 297 mg of uranium
(i.e., 1.8 kg/L * 3.3 L * 50 mg U/kg). Using the 0.1 and 4.5 percent extractable uranium values
from the ORNL study, the calculated uranium solution concentration after three days of leaching is
0.3 and 13 mg/L, respectively. Assuming the uranium forms are similar to the particles present in
the ORNL study and using the calculated upper concentration of 13 mg/L, uranium porewater
concentrations derived from the leaching of uranium particulates (as indicated by lysimeter data) can
exceed the solubility limit of $(UO_2)_2SiO_4 \cdot 2H_2O$, U_3O_7, U_3O_8, U_4O_9, $(UO_2)_3(PO_4)_2 \cdot 4H_2O$, and
$Mg(UO_2)_2(PO_4)_2$ at a pH of 7.2 and Eh of 100 mV if bicarbonate concentrations in the porewater
remain below 300 mg/L. The effect of bicarbonate concentrations on uranium solubility is addressed
in the summary presented below.

F.3.I.4.5 SUMMARY OF URANIUM DISTRIBUTION

330 Dissolution of uranium particles (derived from past releases) and precipitates (derived from leaching
329 of uranium source materials) will occur as undersaturated water percolates through the glacial
overburden. The rate of dissolution will be highly variable and depend on the surface area and
composition of the solid, the pH, Eh, and composition of the water, and the resident time of the
water (i.e., the infiltration rate). As water percolates from the surface to greater depths, total
dissolved solids increase and the concentration of individual ions can have a significant effect on
uranium concentrations (e.g., HCO_3^-). For example, distilled water contacted with FEMP soil in the
ORNL study simulate the conditions in the surface and near surface soil, perched groundwater
analyses represent deeper waters in the water/soil system, and lysimeter data have solute
concentrations between these two end members that serve as an analog of percolating porewater. It is
noted here that the groundwater and lysimeter water are saturated with the carbonate minerals calcite
and dolomite, and that the distilled water used in the ORNL study becomes saturated with these

carbonate minerals within 300 days. Therefore, solubility equilibrium between rainwater and carbonate minerals will be established within a year, and this equilibria is the most important from the standpoint of uranium mobility. A significant factor influencing the uranium concentration in the water/soil system is the increase in HCO_3^- concentration as water moves from the near surface (121 mg/L, ORNL study), to subsurface (310 mg/L, lysimeter data), to the perched groundwater (> 350 mg/L). The geochemical conditions in each of these three zones is discussed with respect to the future distribution of uranium in the glacial overburden.

330   The ORNL study provides analytical data that can be used to estimate the uranium concentrations that may be attainable if rainwater interacts with surface and near-surface soil containing $(UO_2)_3(PO_4)_2 \cdot 4H_2O$ or $CaUO_4$. Based on the ORNL analytical results after 70 days of leaching, EQ3/6 solubility calculations indicate both solutions are supersaturated with the uranium silicate phases haweeite and soddyite and saturated with quartz, while one solution is saturated with calcite, dolomite, and $CaUO_4$ (pH = 7.7, Ca^{+2} = 40.7 mg/L, UO_2^{+2} = 9.5 mg/L, HCO_3^- = 121 mg/L, PO_4^{-2} = 0.12 mg/L) and the other solution is saturated with $(UO_2)_3(PO_4)_2 \cdot 4H_2O$ (pH = 7.1, Ca^{+2} = 31.8 mg/L, UO_2^{+2} = 0.84 mg/L, HCO_3^- = 90 mg/L, PO_4^{-3} = 4.2 mg/L). The predicted supersaturated state for haweeite and soddyite is in agreement with current understanding on the long time periods required to nucleate and precipitate silicate minerals (Lasaga 1981). Saturation of $CaUO_4$ in the B-16 solution indicates that uranium concentrations may reach about 9 mg/L when $CaUO_4$ is present in the glacial overburden and the PO_4^{-3} concentration is kept below 1 mg/L. In contrast, $(UO_2)_3(PO_4)_2 \cdot 4H_2O$ will be stabilized if the PO_4^{-3} concentration increases to about 4 mg/L, resulting in a lower uranium concentration of about 1 mg/L. Therefore, the presence of PO_4^{-3} in moderate concentration will stabilize the more insoluble phase and prolong the time needed to flush uranium from the soil.

330   As water percolates into the subsurface, HCO_3^- concentrations increase as the CO_2 partial pressure in the soil atmosphere rises (Reactions 2 and 3). As the HCO_3^- concentration increases, the CO_3^{-2} concentration also increases and additional uranium can be complexed by Reactions 17 and 18. Therefore, the solubility of uranium solids is enhanced by the formation of uranyl carbonate species and waters containing higher HCO_3^- concentrations have the ability to dissolve and flush more uranium out of the soil. Solubility calculations performed with the lysimeter data indicate $(UO_2)_2SiO_4 \cdot 2H_2O$, U_3O_7, U_3O_8, U_4O_9, $(UO_2)_3(PO_4)_2 \cdot 4H_2O$, and $Mg(UO_2)_2(PO_4)_2$ are saturated in the porewater if the uranium concentration reaches 13 mg/L at a pH of 7.2 and Eh of 100 mV. A

possible drawback of porewater being saturated with one of the indicated uranium phases is that higher uranium concentrations in the water may result in less desorption of uranium. Therefore, if uranium precipitates persist in the subsurface soil, their dissolution will increase the time needed to desorb uranium from underlying soil.

330 Groundwater present in perched bodies within the glacial overburden has the highest observed concentrations of HCO_3^- in the water/glacial overburden system, and therefore the highest observed uranium concentrations. In line with the same arguments presented for the lysimeter data, the increased HCO_3^- concentrations allow a greater portion of the precipitated uranium to be solubilized and carried out of the system. However, the presence of these secondary precipitates in the perched groundwater system will result in less desorption of uranium along the flow path, with the possibility of additional uranium being partitioned onto the soil.

330 In summary, the future distribution of uranium forms will be similar to the present day distribution with the exception of the removed uranium oxide particles from the surface source. Proposed remediation activities are currently calling for a preliminary remediation goal for uranium in glacial overburden of less than or equal to 50 mg/kg. Uranium concentrations in groundwater will be lowered as a result of soil remediation and source removal, and will continually decrease with time as fresh water percolates through the soil and removes uranium by dissolution and desorption. Dissolution of uranium solids will be enhanced as the fresh water increases its HCO_3^- concentration, but the extent of desorption will be suppressed if the dissolution of uranium solids takes place in advance of encountered adsorbed uranium.

F.3.1.5.0 GEOCHEMICAL PARAMETERS FOR FATE AND TRANSPORT MODELING

F.3.1.5.1 DEFINITION OF GEOCHEMICAL PARAMETERS

Available site-specific data on uranium concentrations in soil and aqueous media are used to define the following geochemical parameters used in the Operable Unit 5 fate and transport model.

- K_l — FEMP term defined as the leaching coefficient in units of L/kg. This coefficient is determined using a batch test that contacts waste or contaminated soil with a distilled water solution adjusted to a pH of 5.6 with sulfuric acid. The batch test is run for 15 to 20 days by tumbling the solid and solution in a reaction vessel, and the final solution is analyzed for uranium. A leaching coefficient is calculated by dividing the uranium concentration on the solid (only uranium in excess of background) by the uranium concentration in solution (i.e., mg/kg $\div$ mg/L = L/kg).

- K_l^{calc} — FEMP term defined as the calculated leaching coefficient in units of L/kg. This coefficient represents the in situ leaching coefficient as determined by dividing the uranium concentration for the contaminated soil (only uranium in excess of background) by the uranium concentration in perched groundwater contacting the soil (i.e., mg/kg $\div$ mg/L = L/kg). The calculated leaching coefficient applies to soils in the upper 15 feet of glacial overburden, where weathering and fractures allow particulate uranium to be transported to depth.

- K_d — the adsorption/desorption value or partition coefficient in units of L/kg. The partition coefficient is determined by batch tests that contact soil with spiked uranium solutions (adsorption) and distilled water (desorption). A partition coefficient is calculated by dividing the uranium concentration on the solid (only uranium in excess of background) by the uranium concentration in solution (i.e., mg/kg $\div$ mg/L = L/kg). In general, only an adsorption or desorption value is determined from the batch test and the assumption is made that the reaction is reversible (i.e., adsorption $=$ desorption $= K_d$). These tests are conducted with uncontaminated soil (adsorption) or contaminated soil that are known to contain only adsorbed uranium (desorption).

- K_d^{calc} — the calculated adsorption/desorption value or calculated partition coefficient in units of L/kg. The calculated partition coefficient represents the in situ partition coefficient as determined by dividing the adsorbed uranium concentration for the contaminated soil (only uranium in excess of background) by the uranium concentration in perched groundwater contacting the soil (i.e., mg/kg $\div$ mg/L = L/kg). The calculated partition coefficient applies to soil in unweathered gray till at depths of 15 to 20 feet below the surface, where weathering and fractures are absent and uranium is transported only as a dissolved specie.

- K_e — the extractable uranium present in contaminated soil in units of percent total uranium. This parameter represents the extractable portion of uranium that can be removed from contaminated soil by washing techniques proposed for the Operable Unit 5

FS. Preliminary batch tests indicate 30 to 90 percent of the total uranium present can be extracted using soil washing reagents.

For contaminated soil, a value of K_l can be calculated considering the total or only the extractable contaminant mass in the soil. Value of K_l is lower when only the extractable contaminant mass is considered. For example, when K_e is about 1 percent, the corresponding K_l is usually less than 1 percent of the K_l value based on total contaminant mass. In this RI report, K_e for all the contaminants was assumed to be 100 percent. Therefore, the K_l was based on the total contaminant mass and has a high value for soil outside of the former production area.

The distinction between the parameters K_l and K_d is based on the type of uranium solid that is present in the soil. For K_l, uranium may be present as particulate and adsorbed uranium, and the leaching coefficient measures uranium mobilization due to dissolution and desorption. The K_d is a measurement of adsorption/desorption equilibrium between soil and water, and solid uranium in excess of background is present only as adsorbed uranium.

In the Operable Unit 5 RI Report, the fate and transport model describing uranium migration in the glacial overburden used K_l or K_l^{calc} to define the initial loading of uranium. For example, a kilogram of soil contains 150 mg of uranium and the K_l is determined to be 20 L/kg. Using these values, the first volume of rainwater to move through this soil is estimated to have a uranium concentration of 7.5 mg/L (i.e., 150 mg/kg ÷ 20 L/kg). Each successive pore volume of water will have a lower uranium concentration as the extractable percent of uranium becomes depleted. A calculated depletion curve is used to determine the uranium loading as a function of time. Once uranium is loaded into the aqueous medium and transport begins through the glacial overburden, K_d or K_d^{calc} is used to calculate the uranium retardation factor for the glacial overburden. Further details on the use of these parameters are developed below.

F.3.I.5.2 SITE-SPECIFIC GEOCHEMICAL PARAMETERS

Available information that can be used to assign geochemical parameters for fate and transport modeling include site-specific batch tests with waste materials and contaminated and uncontaminated soil, existing uranium analytical data on glacial overburden and perched groundwater, and pertinent literature studies conducted with similar soil. The current range of site-specific geochemical parameters is given in Table F.3.I.5-1.

For contaminated soil defined as waste materials (Table F.3.I.5-1), the K_1 values range from 12 to
1708 L/kg and K_1^{calc} from 0.6 to 3558 L/kg. This wide range in leaching coefficients reflects both
the variation in solubility of the uranium solids present in the soil (see Table F.3.I.3-2) and the
amount of time adsorbed uranium has been present on the soil particles. Soil (containing soluble
uranium forms (e.g., UF_6) and physically adsorbed uranium (as opposed to chemisorbed uranium)
readily release the uranium to solution, resulting in low leaching coefficients. Conversely, less
soluble uranium particles (e.g., UO_2) and chemisorbed uranium are slowly released to solution,
resulting in high leaching coefficients.

For the Operable Unit 5 fate and transport model, the leaching coefficients that reflect the present
release of uranium from contaminated soil range from 12 to 311 L/kg (Table F.3.I.5-1). This range
is in good agreement with the mean values reported for K_1^{calc} in the production area, with 14 L/kg
representing the soluble uranium forms and 301 L/kg the less soluble uranium solids. Therefore,
uranium loadings in the fate and transport model will be derived using leaching coefficients near 12
L/kg when aqueous spills and/or soluble uranium forms are known or suspected to be present (i.e., in
the Plant 2/3, Plant 6, and Plant 9 areas) and by using values near 311 L/kg when less soluble forms
of uranium are present. This latter condition presently holds for most of the site soil where residual
uranium oxide particles are the dominant source of uranium.

332 In order to present the general geochemical conditions at the FEMP, the areas with low K_1 are
conservatively defined as shown in Figure F.3.4-1. This areal delineation of low K_1 areas considers
the potential uncertainty in the locations of actual boundaries. However, in the Operable Unit 5 FS,
perched groundwater analyses that show elevated uranium concentrations will be mapped to wells in
the production area to delineate the suspected areas of spills and/or leaks in higher resolution. These
perched groundwater plumes will be used with soil data to refine the delineation of low K_1 areas and
to appraise their correlation. The refined delineation will be used to determine extents of required
soil excavation during the cleanup.

After uranium is leached from the source it is free to migrate through the glacial overburden; the fate
and transport model uses K_d or K_d^{calc} to describe the retardation of uranium by the glacial
overburden. Glacial overburden K_d values derived from adsorption batch tests range from 11 to
40 L/kg, with a combined mean of 25 L/kg for the four reported values (Table F.3.I.5-1). The K_d^{calc}
values are grossly different for production area soil associated with aqueous spills (12 to 32 L/kg) as

compared to the soil known to be contaminated solely by release of uranium from surface particles (75 to 2433 L/kg). Discreet ranges of K_d^{calc} for these two areas are interpreted to reflect the difference in surface reaction kinetics associated with adsorption and desorption, as discussed in Section F.3.I.3.0 and conceptualized below.

Leaching of uranium results in a migrating plume away from the source. The front of this plume reaches an underlying soil horizon and the uranium concentration in the plume continues to increase at this horizon as the plume passes through. As long as the surface source is present, the uranium concentration in the plume will increase toward its maximum concentration and adsorption of uranium will be the dominant process at this soil horizon if the maximum concentration (i.e., the peak) of uranium remains below the solubility limit of uranium solids. To illustrate, assume partition-coefficient equilibrium (a tenet of the fate and transport model) between the aqueous and solid phases is given by:

$$\text{adsorbed uranium (mg/kg)} \div \text{aqueous uranium (mg/L)} = 24 \text{ L/kg}$$

where 24 L/kg is the average K_d value for the Operable Unit 2 and Brookhaven National Laboratory (BNL) adsorption studies (Table F.3.I.5-1). As the aqueous uranium concentration increases, uranium must be adsorbed onto the solid to satisfy the partition-coefficient equilibrium. Therefore, desorption is not favored as long as the aqueous uranium concentration is increasing toward the peak concentration.

332 Removal of the uranium source will result in dilution of the uranium plume by fresh infiltrating rainwater, which will lower aqueous uranium concentrations and initiate desorption to satisfy the partition-coefficient equilibrium. However, as noted in Section F.3.I.3.0, desorption values are greater than adsorption values when enough time is available (i.e., decades) for chemisorption to occur because chemisorption imparts a hysteresis to the adsorption/desorption process that prevents desorption of the entire mass of adsorbed uranium. Using the partition-coefficient expression above and the principle of chemisorption, adsorbed uranium will not completely desorb in response to a decreasing aqueous uranium concentration and the partition coefficient must increase to account for the hysteresis phenomenon. Therefore, if the migrating plume takes decades to pass a given horizon of the soil (a common observation), ample time has passed for chemisorption to occur and calculated desorption values will exceed adsorption values.

332   These adsorption and desorption concepts can be applied to glacial overburden in the production area. Glacial overburden soil contaminated by aqueous spills is experiencing active adsorption (12 to 32 L/kg, Table F.3.1.5-1), due to the presence of a soluble uranium source that is leaching uranium concentrations in the plume. Soil contaminated by the release of uranium from air emissions are experiencing desorption (75 to 2433 L/kg, Table F.3.1.5-1), because discreet, limited past releases of soluble particles (e.g., UF_6) have been dissolved by rainwater and the peak concentration from the dissolution of these particles has passed through the overburden (the Operable Unit 5 FS is currently delineating the boundaries for production areas contaminated by aqueous spills and those areas receiving only air emissions). The less soluble uranium oxides remaining on the surface do not leach as readily as uranium fluoride particles, resulting in a decrease in the aqueous uranium concentration in the plume and initiation of the desorption process.

Historical information on uranium releases (Section F.3.1.2.0) supports the conceptual model of adsorption in areas of aqueous spills/leaks versus desorption in areas that received only uranium particles from air emissions. Aqueous spills and leaks occurred on a continuous basis from production activities associated with Plants 2/3, 6, and 9, and these activities have placed a large source of soluble uranium in local areas of the glacial overburden. Air emissions of uranium fluoride and oxide particles cover the entire production area, with uranium oxides comprising about 75 percent of the released mass (Section F.3.1.2.0). As rainwater rapidly dissolved the soluble uranium fluoride particles, the resulting plume reached its maximum uranium concentration quickly and this peak has passed through the glacial overburden in most areas (i.e., desorption is now occurring in these areas). Around Plants 2/3, 6, and 9, the large source of soluble uranium has not been depleted, and the uranium concentration in the migrating plume continues to increase (i.e., adsorption is occurring in these areas). Therefore, adsorption values best describe uranium retardation in areas having soluble uranium sources.

332   Independent evidence for active adsorption in the Plant 2/3, Plant 6, and Plant 9 areas can be found in the adsorption values obtained from the Operable Unit 2 and BNL studies (Table F.3.1.5-1). The average K_d value derived from these adsorption studies is identical to the K_d^{calc} average reported for production area soil contaminated by aqueous spills (i.e., 24 L/kg). Given the Operable Unit 2 and BNL batch-test results and in situ measurements from the production area, a K_d value of 24 L/kg is recommended for the fate and transport model to describe the adsorption of uranium onto glacial overburden, if the migrating plume hasn't reached its peak concentration. When soluble forms of

uranium have been depleted from the source and the plume peak takes decades to pass through the

glacial overburden, larger K_d values are warranted to describe the desorption. The best estimate of

K_d for the fate and transport model when desorption is occurring is the K_d^{calc} geometric mean of 270

L/kg (Table F.3.I.5-1). A sensitivity analysis conducted with the fate and transport model has

bounded the uranium migration using values of 15 and 222 L/kg. The slight difference in these and

the recommended values will produce no significant change in the existing sensitivity analysis.

Numerous uranium adsorption values have been reported in the literature, and a summary by

Sheppard et al. (1984) lists several studies conducted under a variety of conditions that cover a range

of uranium adsorption values from 0.13 to 790,000 L/kg. The studies summarized in Sheppard et al.

(1984) that are most pertinent to the FEMP glacial overburden and Great Miami Aquifer are those of

Rancon (1973) and Yamamoto et al. (1973).

Rancon (1973) studied the adsorption of uranium on carbonate soil and reported uranium adsorption

values of 16 and 33 L/kg, respectively. These values are in good agreement with the Operable Unit 2

and BNL adsorption studies (Table F.3.I.5-1), and indicate that the adsorption behavior of uranium in

carbonate soils is remarkably consistent.

332 Yamamoto et al. (1973) investigated uranium adsorption onto sandy soil from carbonate solutions and

reported uranium adsorption values of 0.13 to 0.25 L/kg. These low values reflect the coarse particle

size (i.e., reduced surface area) and composition (i.e., lack of carbonate minerals, aluminum and iron

oxyhydroxide surfaces, and clay minerals) of the sandy soil and the complexation of uranium by

carbonate ion (Reactions 17 and 18 in Section F.3.I.3.0). Results from this study are close to the

lowest value reported for the saturated sand and gravel aquifer in the south plume area (Table F.3.I.5-

1), and may be appropriate for examining adsorption in the Great Miami Aquifer.

F.3.I.5.3 SUMMARY

Experimental data derived from batch tests, site-specific uranium concentrations in soil and

groundwater, and literature studies are used to define and justify the assignment of geochemical

parameters to the ODAST fate and transport model of the glacial overburden. Leaching of uranium

from near-surface Operable Unit 5 soil sources has been investigated with batch tests and analytical

measurements on site-specific soil and groundwater samples to define the 12 to 311 L/kg range for K_l

and K_l^{calc} values. The K_l and K_l^{calc} values are used to develop uranium loading curves as a function

of time, and these curves are used as input data to the fate and transport model. The large range in K_1 and K_1^{calc} values reflects the heterogeneity of uranium forms in the contaminated soil.

Adsorption batch tests, uranium analyses of site-specific soil and groundwater samples, and literature studies indicate that the adsorption of uranium onto glacial overburden soil is best defined using a K_d value of 24 L/kg. The uniform range of adsorption values for several independent studies reflects the homogeneous distribution of uranyl carbonate species in the groundwater/glacial overburden environment. Desorption of uranium will occur when the plume peak has passed through the overburden or when the uranium source is removed from the glacial overburden, and a K_d value as high as 270 L/kg may be used to model the desorption of uranium. A large range in the observed desorption values (75 to 2433 L/kg) reflects chemisorption of uranium by the soil particle surface; with chemisorption favored by increasing residence time. Modeling a desorption scenario will apply to source areas depleted of their soluble uranium or areas where the source is excavated and removed.

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TABLE F.3.1.5-1

RANGE OF SITE-SPECIFIC GEOCHEMICAL PARAMETERS

Media	Parameter (L/kg)	Range
Waste Materials		
Plant 2/3, Plant 6, and Plant 9 contaminated soil	K_l^{calc}	0.6 - 8.35[a] (14[b])
Remaining production area contaminated soil	K_l^{calc}	75 - 3,558[a] (301[b])
OU2 waste	K_l	37 - 177[c]
OU2 contaminated soil	K_l	200 - 280[c]
OU4 contaminated soil	K_l	12 - 15[c]
OU5 contaminated soil	K_l	12 - 311[d]
Contaminated soil studied by Oak Ridge National Laboratory	K_l	64 - 1708[e]
Glacial Overburden		
OU2 soil	Adsorption K_d	11 - 40[c]
BNL study	Adsorption K_d	23 - 25[f]
Production area subsurface soil contaminated by aqueous spills	Adsorption K_d^{calc}	12 - 32[g] (24[h])
Production area subsurface soil contaminated by air emissions	Desorption K_d^{calc}	75 - 2,433[g] (270[b])
Unsaturated Sand and Gravel		
OU2 South Field	K_d	10 - 12[c]
Saturated Sand and Gravel		
OU1 waste pit area	K_d^{calc}	2 - 68[i] (14[b])
OU2 South Field	K_d	6 - 9[c]
South Plume area	K_d^{calc}	0.8 - 4.4[i] (2.7[h])
Calibration of SWIFT model	K_d^{calc}	1.8

[a]Production area soil contaminated by uranium releases, as indicated in Table F.3.II.3-3.
[b]Geometric mean for indicated range.
[c]DOE (1993c). K_l determined from 17-day batch test with deionized water at initial pH of 5.6. Adsorption K_d determined from 17-day batch test with spiked solution.
[d]Unpublished preliminary results from OU5 soil washing studies. K_l determined from 17-day batch test with deionized water at initial pH of 5.6.
[e]Lee et al. (1993). K_l determined from 21-day batch test with deionized water.
[f]IT (1993). K_d determined from 60-day batch test with spiked perched groundwater.
[g]Production area subsurface soil between 15 and 20 feet below the surface contaminated by uranium releases, as indicated by Wells 1348, 1354, 1360, 1266, 1317, 1341, 1225, 1230, and 1250 in Table F.3.II.
[h]Arithmetic mean for indicated range.
[i]DOE (1993a). Appendix A, Issue 3 and 5 Report.

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LEGEND:

— · · — · · — COUNTY LINE

— — — — — FEMP BOUNDARY

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SCALE

1400   700   0   1400 FEET

FIGURE F.3.1.2-1. MAJOR FEATURES OF THE FEMP 101197

ORE CONCENTRATES, RECYCLED URANIUM COMPOUNDS, METAL & RESIDUES FROM OFF SITE

```
                    ┌─────────────┐
                    │  RECEIVE,   │
                    │  EVALUATE   │                          PLANT 1
                    │  & STORE    │
                    └─────────────┘
```

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┌──────────┐   ┌──────────┐   ┌────────────┐   ┌──────────┐
│   DRUM   │   │  METAL   │   │ CONTINUOUS │   │ DIGESTION│
│ DIGESTION│   │ DISSOLVER│   │  DIGESTION │   │          │
└──────────┘   └──────────┘   └────────────┘   └──────────┘
                         CRUDE        UNH    NEUTRALIZED LEACHED    PLANT 2
                                             MgF₂ CAKE SLURRY
                                                TO WET              SLUG LEACH
┌──────────┐   ┌──────────┐                  CHEMICAL
│ SOLVENT  │◄──│ SOLVENT  │                  WASTE PITS
│ RECOVERY │   │EXTRACTION│
└──────────┘   └──────────┘
                      NEUTRALIZED RAFFINATE TO GENERAL SUMP
```

TAIL GAS ◄──
(NO_2 + H_2O)   ┌──────────┐ NO_2 ┌────────────┐
                     │HNO_3 ACID│◄────────│EVAPORATION &│
                     │ RECOVERY │ H_2O │ DENITRATION │   PLANT 3
RECOVERED ACID   └──────────┘   └────────────┘

CASCADE FEED ◄──────────────────── UO_3

```
                ┌──────────┐  $N_2$  ┌──────────┐  TAIL GAS
$NH_3$ ──────►  │  HH₃     │────────►│  ORANGE  │  $NO_2$ + $H_2O$
                │DISSOCIATOR│ $2H_2$ │  OXIDE   │
                └──────────┘         │ REDUCTION│   $H_2O$  CaO   TAIL GAS
                                     └──────────┘               ($H_2O$ + HF)
                ┌──────────┐         ┌──────────┐
                │  HYDRO-  │────────►│    HF    │   35% HF       PLANT 4
                │FLUORINATION│       │ RECOVERY │   SOLUTION
                └──────────┘         └──────────┘   OFFSITE
                                                    DISPOSITION
```

REFINERY FEEDS

```
                OPERATE UF₄                ┌──────┐   ┌────────┐   OFFSITE
                (DEPLETED)                 │ UF₄  │◄──│UF₆ TO UF₄│  UF₆
                                           └──────┘   │ PROCESS │
        ┌──────────┐       ┌──────────┐               └────────┘   PLANT 7
PLANT   │  SCRAP   │       │  METAL   │                            AND PILOT
8       │ RECOVERY │       │ REDUCTION│                            PLANT
        └──────────┘       └──────────┘
                                                      PLANT 5
              TO DRY CHEMICAL
              WASTE PIT        DERBIES
        TAILINGS
                          ┌──────────┐
                          │  METAL   │
                          │ CASTING  │
                          └──────────┘
        RESIDUES              INGOTS                  PLANT 6
                          ┌──────────┐                AND 9
                          │  METAL   │
                          │ ROLLING  │
                          └──────────┘                REMELT METAL
                                     RODS
        METAL EXTRUSION         TUBES
        OFF SITE
                          ┌──────────┐
                          │  METAL   │
                          │ MACHINING│
                          └──────────┘
        ┌────────┐   ┌────────┐
        │TO WASTE│   │BILLETS TO│
        │ PITS   │   │REACTOR   │
        └────────┘   │ SITES    │    FINISHED FUEL CORES & BILLETS TO REACTOR SITE
                     └────────┘
```

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FIGURE F.3.I.2-3. URANIUM METAL PROCESS DIAGRAM

t = past

t = present

t = future

U_3O_8, UO_2, UO_3, UO_3:$2H_2O$, $(UO_2)_3(PO_4)_2 \cdot 4H_2O$?, $Mg(UO_2)_2(PO_4)_2$?, $CaUO_4$?

Remediated Soil

$UO_2(NO_3)_2 \cdot 6H_2O$, UF_6, UF_4, $Na_2U_2O_7$, U_3O_8, UO_2, UO_3

Primary Sources

Brown Glacial Overburden

Gray Glacial Overburden

Uranyl Nitrate Ammonium Uranate, and other Uranium Solutions. Dissolution of Glacial Overburden Minerals and Possible Precipitation of $(UO_2)_3(PO_4)_2 \cdot 4H_2O$, $Mg(UO_2)_2(PO_4)_2$, $CaUO_4$, and/or $UO_3 \cdot 2H_2O$

Aqueous $UO_2(CO_3)_2^{-2}$, $UO_2(CO_3)_3^{-4}$, $(UO_2)_2CO_3(OH)_3^-$, $UO_2(OH)_2^0$, and $UO_2PO_4^-$ Derived from Reaction of Spilled Solutions With Glacial Overburden Minerals

Possible Precipitates of $(UO_2)_3(PO_4)_2 \cdot 4H_2O$, $Mg(UO_2)_2(PO_4)_2$, $CaUO_4$, and/or $UO_3 \cdot 2H_2O$

Aqueous $UO_2(CO_3)_2^{-2}$, $UO_2(CO_3)_3^{-4}$, $(UO_2)_2CO_3(OH)_3^-$, $UO_2(OH)_2^0$, and $UO_2PO_4^-$ Derived from Desorption of Uranium and Possible Dissolution of $(UO_2)_3(PO_4)_2 \cdot 4H_2O$, $Mg(UO_2)_2(PO_4)_2$, $CaUO_4$, and/or $UO_3 \cdot 2H_2O$

Aqueous $UO_2(CO_3)_2^{-2}$, $UO_2(CO_3)_3^{-4}$, $(UO_2)_2CO_3(OH)_3^-$, $UO_2(OH)_2^0$, and $UO_2PO_4^-$ and Adsorbed Uranium Derived Primarily from Dissolution of $UO_2(NO_3) \cdot 6H_2O$, UF_6, UF_4, and $Na_2U_2O_7$, Some Uranium Derived from Dissolution of U_3O_8, UO_2, $UO_3 \cdot 2H_2O$, $(UO_2)_2(PO_4)_3 \cdot 4H_2O$?, $Mg(UO_2)_2(PO_4)_2$?, and/$CaUO_4$?

a

b

c

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FIGURE F.3.I.4-1   URANIUM DISTRIBUTION RESULTING FROM AQUEOUS AND PARTICULATE SOURCES

t = past

UF$_6$, UF$_4$, Na$_2$U$_2$O$_7$, U$_3$O$_8$, UO$_2$, UO$_3$

Primary Source

Brown
Glacial
Overburden

Aqueous UO$_2$(CO$_3$)$_2$$^{-2}$,
UO$_2$(CO$_3$)$_3$$^{-4}$,
(UO$_2$)$_2$CO$_3$(OH)$_3$$^-$,
UO$_2$(OH)$_2$^{0}, and
UO$_2$PO$_4$$^-$ and Adsorbed
Uranium Derived Primarily from
Dissolution of UO$_2$(NO$_3$)$_2$·6H$_2$O,
UF$_6$,UF$_4$,and Na$_2$U$_2$O$_7$,
Some Uranium Derived from
Dissolution of U$_3$O$_8$, UO$_2$, UO$_3$,
(UO$_2$)$_2$(PO$_4$)$_3$·4H$_2$O?,
Mg(UO$_2$)$_2$(PO$_4$)$_2$?, and/or CaUO$_4$?

Gray
Glacial
Overburden

a

t = present

U$_3$O$_8$, UO$_2$, UO$_3$,UO$_3$·2H$_2$O,
(UO$_2$)$_3$(PO$_4$)$_2$·4H$_2$0?,
Mg(UO$_2$)$_2$(PO$_4$)$_2$?, CaUO$_4$?

Possible Precipitates of
(UO$_2$)$_3$(PO$_4$)$_2$·4H$_2$O,
Mg(UO$_2$)$_2$(PO$_4$)$_2$, CaUO$_4$,
and/or UO$_3$·2H$_2$O

Aqueous UO$_2$(CO$_3$)$_2$$^{-2}$,
UO$_2$(CO$_3$)$_3$$^{-4}$,
(UO$_2$)$_2$CO$_3$(OH)$_3$$^-$,
UO$_2$(OH)$_2$^{0}, and
UO$_2$PO$_4$$^-$Derived from
Desorption of Uranium and
Possible Dissolution of
(UO$_2$)$_3$(PO$_4$)$_2$·4H$_2$O,
Mg(UO$_2$)$_2$(PO$_4$)$_2$, CaUO$_4$,
and/or UO$_3$·2H$_2$O

Aqueous UO$_2$(CO$_3$)$_2$$^{-2}$,
UO$_2$(CO$_3$)$_3$$^{-4}$,
(UO$_2$)$_2$CO$_3$(OH)$_3$$^-$,
UO$_2$(OH)$_2$^{0}, and
UO$_2$PO$_4$$^-$and Adsorbed
Uranium Derived Primarily from
Dissolution of UO$_2$(NO$_3$)·6H$_2$O,
UF$_6$,UF$_4$,and Na$_2$U$_2$O$_7$,
Some Uranium Derived from
Dissolution of U$_3$O$_8$, UO$_2$, UO$_3$·2H$_2$O,
(UO$_2$)$_2$(PO$_4$)$_3$·4H$_2$O?,
Mg(UO$_2$)$_2$(PO$_4$)$_2$?, and/or CaUO$_4$?

b

t = future

Remediated Soil

c

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FIGURE F.3.I.4-2 URANIUM DISTRIBUTION ⬤TING FROM PARTICULATE SOURCES